IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	**Wang et al.**
Application No.:	**10/797996**
Filed:	**March 11, 2004**
For:	**Balloon Structure With PTFE Component**
Examiner:	**Matthew J. Daniels**
Group Art Unit:	**1732**

Mail Stop <u>Appeal Brief-Patents</u>
Commissioner for Patents   **Docket No.: S63.2Q-7182-US02**
P.O. Box 1450
Alexandria, VA 22313-1450

SUPPLEMENTAL BRIEF ON APPEAL

This is a Revised Brief on Appeal for the above-identified application is in response to the Notice of Non-Compliant Appeal Brief dated February 5, 2008, in which claims 18 and 23-26 are pending have been twice or finally rejected. Heading (vi) has been amended.

A Notice of Appeal was filed in this case on November 16, 2007. The fees required under §1.17(c) for filing this brief were addressed in the Notice of Appeal. The Commissioner is authorized to charge Deposit Account 22-0350 for any other fees which may be due with this appeal.

(i)   Real Party in Interest

          The application is assigned to Boston Scientific Scimed, Inc., formerly known as

Scimed Life Systems, Inc., One SciMed Place, Maple Grove, MN 55311-1566, a Minnesota

Corporation and a subsidiary of Boston Scientific Corporation, One Boston Scientific Place,

Natick, Massachusetts, 01760-1537, a Delaware Corporation.

(ii)   Related Appeals and Interferences

          None.

(iii)   Status of Claims

          Claims 18 and 23-26 are pending in this application and have been twice or finally

rejected and are the subject of this appeal. Claims 1-17, 19-22 and 27-39 have been canceled.

(iv)   Status of Amendments

          All amendments have been entered to date. A Notice of Appeal and Reasons for

Pre-Appeal Conference paper were filed on November 16, 2007. A Notice of Panel Decision

from Pre-Appeal Brief Review was mailed December 12, 2007. No claims were allowed.

(v)   Summary of Claimed Subject Matter

          A summary of representative independent claims, as required by 37 C.F.R.

§41.37(c)(1)(v), and a non-limiting listing of locations where support may be found [bracketed

citations] is provided as follows:

          Independent claim 18 is directed to a method of forming a balloon having at least

three layers, the method including providing first, second and third tubes, the second tube formed

of a tube made of a material selected from the group consisting of fluoropolymers and high

density polyethylene, inserting the first tube into the second tube, inserting the second tube into

the third tube, inserting the first, second and third tubes into a balloon mold and expanding the

first, second and third tubes at a desired temperature so as to form a balloon [page 7, 4th full

paragraph, claim 18 as originally filed].

Independent claim 23 is directed to a method of forming a balloon having at least

three layers, the method including providing first, second and third tubes, the second tube formed

of expanded PTFE, inserting the first tube into the second tube, inserting the second tube into the

third tube, laminating the first tube and the second tube together, and laminating the second tube

and third tube together so as to form at least a three tube laminate [page 7, 4th full paragraph,

claim 23 as originally filed].

(vi)   Grounds of Rejection to be Reviewed on Appeal

I.   Whether the Examiner erred in rejecting claims 18 and 23-26 under 35

U.S.C. §103(a) as being unpatentable over Crocker (USPN 5843116) in view of Gore (USPN

3953566).

(vii)   Argument

A.   Brief Summary

I.   Applicants submit that the Examiner erred in rejecting claims 18 and 23-26

under 35 U.S.C. §103(a) as being unpatentable over Crocker et al. (USPN 5843116) in view of

Gore (USPN 3953566).

B.   **Detailed Argument**

<u>Claim 18</u>

Independent claim 18 of the present application is directed to a method of making a balloon wherein the balloon has at least three layers, the method including providing first, second and third tubes, *the second tube formed of a tube made of a material selected from the group consisting of fluoropolymers and high density polyethylene.*

As admitted in the Final Office Action dated July 16, 2007, "Crocker....[is] silent as to the second tube formed of a tube made of a material selected from the group consisting of fluoropolymers and high density polyethylene." Final Office Action, page 3.

It is further asserted that because "Crocker…suggests cross-linked polyethylene (5:35-39), … it is the Examiner's position that crosslinking would produce a polyethylene having a "high density", as claimed."

This is simply incorrect.

Applicants submit that crosslinking the polyethylene disclosed by Crocker does not produce the "high density" polyethylene as disclosed and claimed in the present application.

Applicants have argued in their last two responses, as well as in the Pre-Appeal Conference Brief, and continue to maintain, that the cross-linked polyethylene disclosed by Crocker et al., is different than "high density polyethylene", and that cross-linked polyethylene is a polyethylene that has been subsequently modified by linking its molecules in a manner which changes the material from a thermoplastic to a thermoset, two distinctly different classes of polymer materials, and not readily substitutes for one another.

In the Final Office Action dated July 16, 2007, it was asserted that:

a) Applicants' position rests on the use of a relative term which is not

differentiated in the specification by any material characteristics. Therefore, it is submitted that the reference provides a "high density" polyethylene, or that a high density polyethylene is produced as a result of crosslinking, and that the rejection based thereon is valid. It is submitted that it is not implicit that high density polyethylene is thermoplastic (or remains a thermoplastic material), as asserted by Applicants' arguments. See, for example, USPN 3376238 to Gregorian, which teaches providing a commercially available polyethylene, and crosslinking, providing a crosslinked high density polyethylene (7:15-25, also see Example 1). Therefore, the asserted thermoplastic nature of the high density polyethylene, which does not appear to be supported by the specification and is not commensurate with the scope of the claim, is not sufficient to distinguish the claimed invention.

Office Action, pages 5-6, section 6.

This is incorrect. First, Applicants have differentiated the "high density" polyethylene and the PTFE disclosed therein as those materials having "a node structure connected by multiple fibers." Page 5, 5th paragraph of the present Specification. Suitable materials include expanded PTFE and high density polyethylene.

Second, simply using the term "high density polyethylene" is enough to differentiate the material not only from thermoset polyethylene as disclosed by Crocker et al., but from other types of thermoplastic polyethylene as well. For example, as opposed to "low density", "linear low density", "medium density", and "crosslinked" or thermoset polyethylene. *As is notoriously well known*, each of these terms has a specific meaning to those of ordinary skill in the art, each referring to a different polyethylene material having different characteristics. See attached MatWeb overview of high density polyethylene clearly illustrating it is understood to be thermoplastic, not thermoset.

Thus, the term "high density polyethylene" has particular meaning to a skilled person as a sub-group of *thermoplastic* polyethylene polymers. See attached MatWeb overview of high density polyethylene. Gregorian is not to the contrary. Gregorian starts with a

thermoplastic polyethylene that is already high density polyethylene (0.96 g/cc). Gregorian then

crosslinks and treats with acid to produce a different material namely "crosslinked, microporous,

high density polyethylene." Any person of skill in the art recognizes that the crosslinked material

is no longer the same as the material known in the art as "high density polyethylene."

Even more to the point of the rejection, it is clear from Gregorian taken with the

Matweb Overview, that the "high density" characterization in Gregorian's Example 2 comes from

the fact that the *starting material* is high density polyethylene, not because of the crosslinking.

Applicants submit that crosslinking is not an inherent characteristic of a

polyethylene. Furthermore, applicants describe methods of making the balloons of the present

application beginning on page 6, 4th full paragraph to page 8, 1st full paragraph. Nowhere is it

disclosed that the polymer materials employed in these methods are crosslinked. Applicants

silence as to crosslinking and the description in the present specification as to how the balloons

are being formed are sufficient to convey to those of ordinary skill in the art that the high density

polyethylene disclosed and claimed therein is the conventionally known thermoplastic material,

not a thermoset material.

It was further asserted in the Final Office Action that "…in the alternative, Gore

teaches a PTFE (a fluoropolymer) tubular product (14: 17-20) having a dense structure and

extremely high strength which would have been suitable for use in Crocker's method as the

expansion limiting bands (Crocker, 5:28-30)." Final Office Action, July 16, 2007, page 3.

Thus, a second source of disagreement is whether or not Gore's PTFE would have

been suitable for use in Crocker's method as the expansion limiting bands (Crocker, 5:28-30)."

Again, Applicant's disagree.

First, it is incorrect to state that the PTFE product of Gore has a dense structure.

This is contrary to what Gore discloses regarding the PTFE. Gore describes the PTFE disclosed therein, as "a tetrafluoroethylene polymer in *porous* form which has an amorphous content exceeding about 5% and which has a micro-structure characterized by nodes interconnected by fibrils." Gore, US 3,953,566, Abstract. An alternative description for this material is expanded PTFE. See, for example, Gore, column 5, lines 47-58.

Clearly, the Gore PTFE is "porous" and not "dense" as asserted in the Final Office Action.

There is nothing in Crocker et al. that would lead one of skill in the art to employ the *porous* PTFE disclosed by Gore for forming the expansion limiting bands 40, 44 of Crocker et al.

Crocker et al. describe the expansion limiting bands 40, 44 disclosed therein, as being "nondistensible". See col. 5, lines 20-39. One way to provide the desired "expansion limiting characteristics" is to form the expansion limiting bands 40, 44 from nondistensible materials. One example is polyester. See col. 5, lines 32-36. Examples of other generally nondistensible materials given by Crocker et al. include "...nylon, polyamide, Kevlar fiber, cross-linked polyethylene, polyethylene terephthalate..." Polytetrafluoroethylene is not suggested by Crocker et al. as being a material that is nondistensible, and that would provide the desired expansion limiting characteristics to the expansion limiting bands 40, 44.

Gore discloses "a tetrafluoroethylene polymer in porous form which has an amorphous content exceeding about 5% and which has a micro-structure characterized by nodes interconnected by fibrils." Gore, US 3,953,566, Abstract. There is no disclosure as to any expansion limiting characteristics of PTFE and Gore fails to describe the specific PTFE material employed therein as being either inelastic or nondistensible.

Crocker et al. provides no basis for selecting PTFE, and one of ordinary skill in the art would not be lead to conclude that the PTFE tube disclosed by Gore would indeed be a suitable substitute for the expansion limiting bands disclosed by Crocker et al.

Even after *KSR*, there must be some motivation to substitute the Gore material for those disclosed by Crocker et al. as being suitable for the nondistensible expansion limiting bands. Under *KSR*, one of ordinary skill in the art must be able to readily recognize a benefit of modifying the balloon disclosed by Crocker et al. with the porous PTFE material disclosed by Gore in order to render claim 18 obvious over this combination. If one of skill in the art cannot implement a predictable variation, or see the benefit of doing so, the combination does not preclude patentability under 35 U.S.C. §103(a). See *KSR International v. Teleflex Inc.*, U.S. Supreme Court No. 04-1350 (April 30, 2007). Applicants submit that the benefit in making this combination is not readily apparent, and that claim 18 is therefore not rendered obvious over Crocker et al. in view of Gore.

Applicants submit that combining Gore with Crocket al. and thus substituting the porous PTFE disclosed by Gore for the nondistensible materials of Crocker et al. would be done only with the use impermissible hindsight, employing Applicants' invention as a road map. Hindsight reasoning is impermissible. See *In re Fritch*, 23 USPQ2D 1780, 1784 (Fed. Cir. 1992).

In making a rejection, it is simply not good enough to pick and choose elements randomly from prior art references. Even after *KSR*, there must be some motivation to combine the references. "The TSM test captures a helpful insight: A patent composed of several elements is not proved obvious merely by demonstrating that each element was, independently, known in the prior art." *KSR International v. Teleflex Inc.*, U.S. Supreme Court No. 04-1350 (April 30, 2007).

<u>Claims 23-26</u>

Independent claim 23 also recites, among other features, "…providing first, second and third tubes, the second tube formed of expanded PTFE…."

Claim 23 is not obvious over the combination of Crocker et al. and Gore for at least the reasons that claim 18 is not obvious over the combination of Crocker et al. and Gore. Crocker et al. fails to disclose PTFE as being an expansion limiting, nondistensible material as required for making the expansion limiting bands disclosed therein, and there is no apparent benefit to selecting the PTFE disclosed by Gore as a substitute for the nondistensible materials disclosed by Crocker et al. for use in making the expansion limiting bands.

Claims 24-26 depend from claim 23 and are not obvious over this combination for at least the reasons that claims 18 and 23 are not obvious over this combination.

CONCLUSION

Reversal of the rejection of claims 18 and 23-26 under 35 U.S.C. §103(a) as being

obvious over Crocker et al. in view of Gore is respectfully requested. For at least the reasons

discussed above claims 18 and 23-26 of the instant application, are patentably distinct over the

cited art.

Respectfully submitted,

VIDAS, ARRETT & STEINKRAUS

Date: <u>February 26, 2008</u>   By: <u>/Lisa Ryan-Lindquist/</u>
                                            Lisa R. Lindquist
                                            Registration No.: 43071

6640 Shady Oak Road, Suite 400
Eden Prairie, MN 55344
Telephone: (952) 563-3000
Facsimile: (952) 563-3001
f:\wpwork\lrl\07182US01_appealbrief_20080110.doc

viii. Claims appendix

18. (Previously Presented)   A method of forming a balloon comprising at least three layers

comprising the steps of:

      i)   providing first, second and third tubes, the second tube formed of a tube

made of a material selected from the group consisting of fluoropolymers and high density

polyethylene;

      ii)   inserting the first tube into the second tube;

      iii)   inserting the second tube into the third tube;

      iv)   inserting the first, second and third tubes into a balloon mold;

      v)   expanding the first, second and third tubes at a desired temperature so as to

form a balloon.

23. (Previously Presented)   A method of forming a balloon comprising at least three layers

comprising the steps of:

      i)   providing first, second and third tubes, the second tube formed of

expanded PTFE;

      ii)   inserting the first tube into the second tube;

      iii)   inserting the second tube into the third tube;

      iv)   laminating the first tube and the second tube together;

      v)   laminating the second tube and third tube together so as to form at least a

three tube laminate.

24. (Original) The method of claim 23 further comprising the step of laminating the first and third

tubes together at least in part.

25. (Original) The method of claim 23 further comprising the step of blowing the laminate at a

predetermined temperature.

26. (Original) The method of claim 25 wherein the first and second tubes and the second and

third tubes delaminate upon blowing the balloon.

(ix)   Related Proceedings Appendix

N/A

(x)   Evidence Appendix

MatWeb, The Online Materials Database

Overview - High Density Polyethylene (HDPE), Extruded

Subcategory: HDPE; Polyethylene; Polymer; Thermoplastic

Close Analogs:
Click button for specific proprietary grades that belong to this Overview class.

Proprietary Grades

Please be aware that some proprietary polymers may not be listed because they fall into more than one class or because of ambiguity in manufacturer's information.

Key Words: Plastics, Polymers

The property data has been taken from proprietary materials in the MatWeb database. Each property value reported is the average of appropriate MatWeb entries and the comments report the maximum, minimum, and number of data points used to calculate the value. The values are not necessarily typical of any specific grade, especially less common values and those that can be most affected by additives or processing methods.

Physical Properties	Metric	English	Comments
Density	0.936 - 0.962 g/cc	0.0338 - 0.0348 lb/in³	Average = 0.948 g/cc; Grade Count = 21
Apparent Bulk Density	0.58 - 0.61 g/cc	0.021 - 0.022 lb/in³	Average = 0.59 g/cc; Grade Count=4
Water Absorption	0.01 %	0.01 %	Grade Count = 1
Moisture Vapor Transmission	0.38 cc-mm/m²-24hr-atm	0.965 cc-mil/100 in²-24hr-atm	Grade Count = 1
Environmental Stress Crack Resistance	10 - 5000 hour	10 - 5000 hour	Average = 1600 hr; Grade Count = 16
Melt Flow	0.14 - 13 g/10 min	0.14 - 13 g/10 min	Average = 3.6 g/10 min; Grade Count = 21

Mechanical Properties	Metric	English	Comments
Hardness, Shore D	58 - 65	58 - 65	Average = 62; Grade Count = 14
Tensile Strength, Ultimate	24 - 45 MPa	3480 - 6530 psi	Average = 30 MPa; Grade Count = 9

Tensile Strength, Yield	15 - 30 MPa	2180 - 4350 psi	Average = 21.9 MPa; Grade Count = 15
Elongation at Break	500 - 1000 %	500 - 1000 %	Average = 840%; Grade Count = 17
Tensile Modulus	0.8 - 0.99 GPa	116 - 144 ksi	Average = 0.86 GPa; Grade Count = 3
Flexural Modulus	0.5 - 1.52 GPa	72.5 - 220 ksi	Average = 0.928 GPa; Grade Count = 16
Izod Impact, Notched	0.8 - 7.5 J/cm	1.5 - 14.1 ft-lb/in	Average = 3.7 J/cm; Grade Count = 6
Tensile Impact Strength	320 - 480 kJ/m²	152 - 228 ft-lb/in²	Average = 380 kJ/m²; Grade Count = 3
Coefficient of Friction	0.28	0.28	Grade Count=1

Electrical Properties

Electrical Resistivity	1e+017 ohm-cm	1e+017 ohm-cm	Grade Count = 2
Surface Resistance	1e+017 ohm	1e+017 ohm	Grade Count = 1
Dielectric Constant	2.3	2.3	Grade Count = 2
Dissipation Factor	0.0001 - 0.0005	0.0001 - 0.0005	Average = 0.0003; Grade Count = 2

Thermal Properties

CTE, linear 20°C	140 µm/m-°C	77.8 µin/in-°F	Grade Count=3
Melting Point	124 - 131 °C	255 - 268 °F	Average = 130°C; Grade Count = 9
Vicat Softening Point	108 - 129 °C	226 - 264 °F	Average = 120°C; Grade Count = 15

| Brittleness Temperature | -100 - -70 °C | -148 - -94 °F | Average = -86.2°C; Grade Count=16 |

Processing Properties

| Processing Temperature | 180 - 315 °C | 356 - 599 °F | Average = 210°C; Grade Count = 17 |

US005843116A

United States Patent [19]

Crocker et al.

[11] Patent Number: 5,843,116

[45] Date of Patent: *Dec. 1, 1998

[54] **FOCALIZED INTRALUMINAL BALLOONS**

[75] Inventors: **Michael Crocker**, Anaheim; **Lynn M. Shimada**, Irvine, both of Calif.

[73] Assignee: **Cardiovascular Dynamics, Inc.**, Irvine, Calif.

[*] Notice: The term of this patent shall not extend beyond the expiration date of Pat. No. 5,470,313.

[21] Appl. No.: **742,437**

[22] Filed: **Oct. 30, 1996**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 670,683, Jun. 26, 1996, which is a continuation-in-part of Ser. No. 640,533, May 2, 1996, Pat. No. 5,645,560.

[51] **Int. Cl.**^{6} **A61M 29/08**
[52] **U.S. Cl.** **606/192**; 606/108; 604/96
[58] **Field of Search** 606/194, 192, 606/198, 108; 604/96

[56] **References Cited**

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Primary Examiner—Michael Powell Buiz
Assistant Examiner—Kevin Troung
Attorney, Agent, or Firm—Knobbe, Martens, Olson & Bear, LLP

[57] **ABSTRACT**

Disclosed is a focal balloon having at least one reference zone and a focal zone. In one embodiment, the reference zone and focal zone are inflatable to a first generally cylindrical profile at a first pressure. At a second, greater pressure, the focal section expands to a second, greater diameter, while the reference zone remains substantially at the first diameter. In an alternate embodiment, the focal zone and the reference zone are inflatable to their respective predetermined diameters at the inflation pressure, in the absence of constricting lesions or anatomical structures. Multiple lobed and drug delivery embodiments are also disclosed.

2 Claims, 12 Drawing Sheets
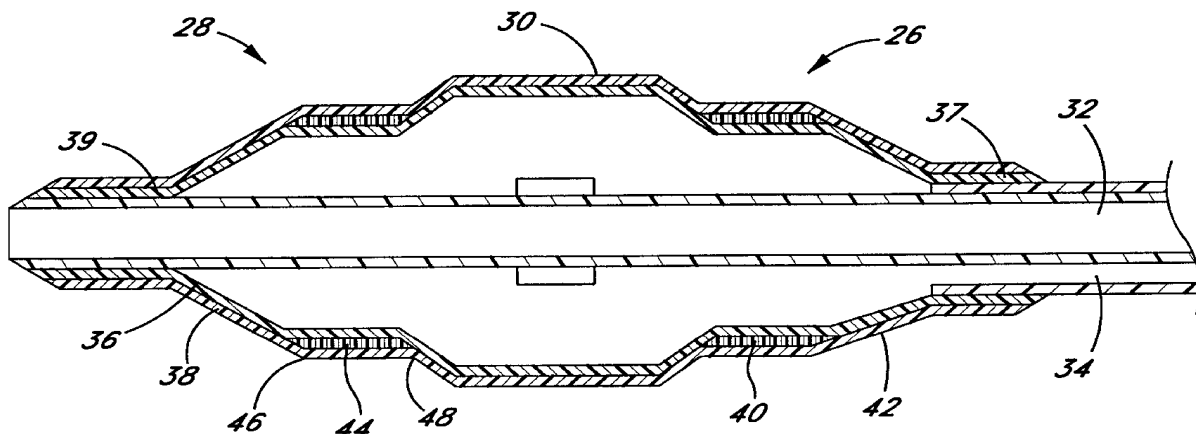
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5,632,762   5/1997 Myler .
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FIG.1

FIG.4

FIG.2

FIG.3

FIG. 5

3.5mm FOCAL BALLOON

——————— BALLOON CENTER (PE)
- - - - - - - BALLOON ENDS (PET)

FIG. 6

FIG.7

FIG. 8

FIG. 9

FIG. 10

FIG. 11

FIG. 12

FIG. 13

FIG. 14

FIG. 15

FIG. 16

FIG. 17

FIG. 18
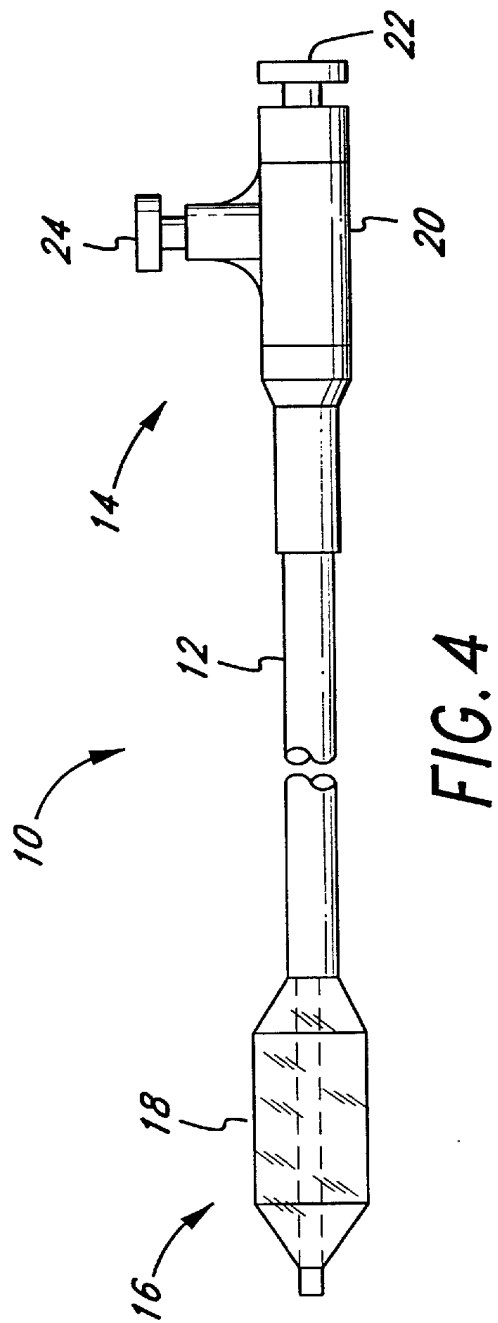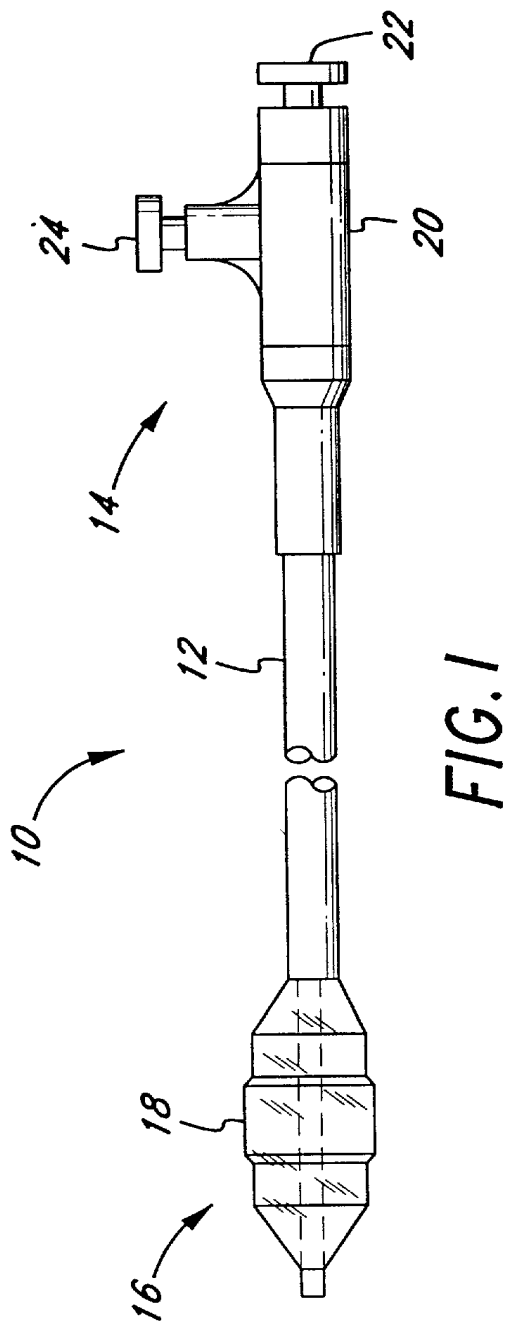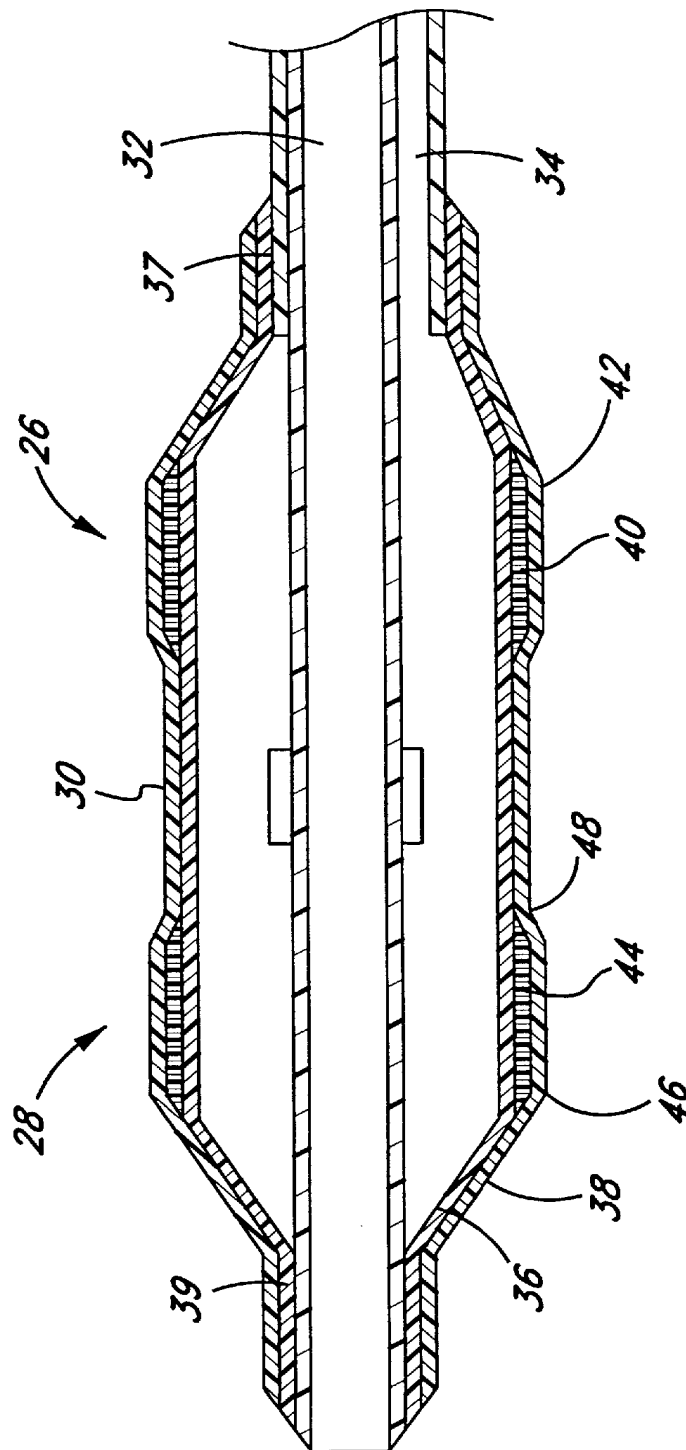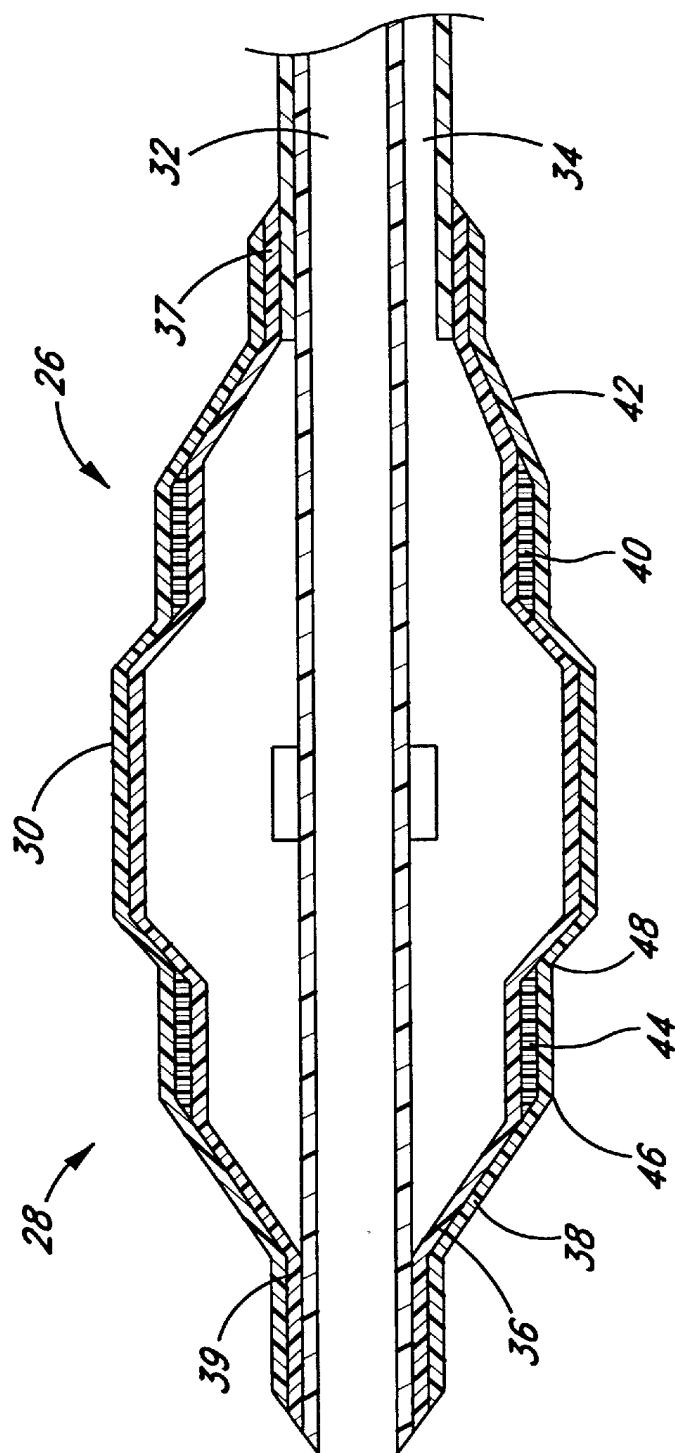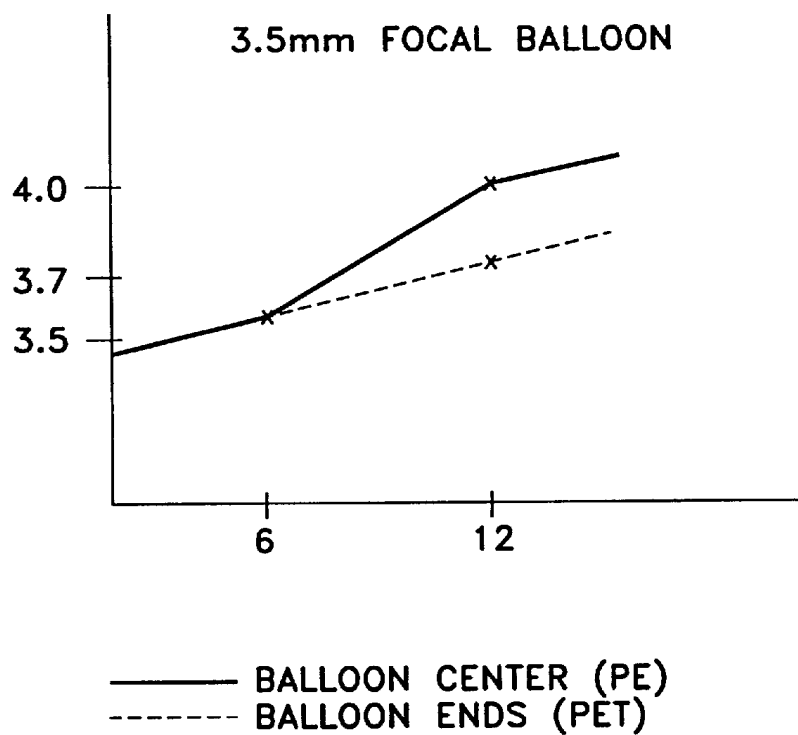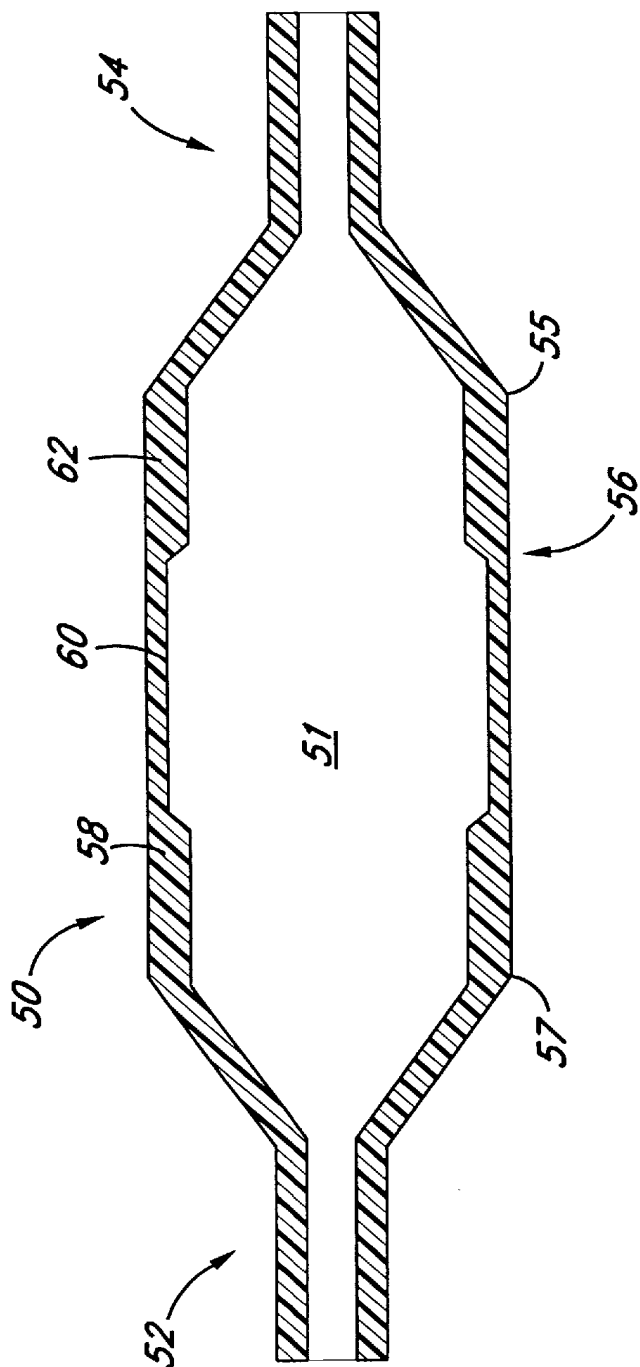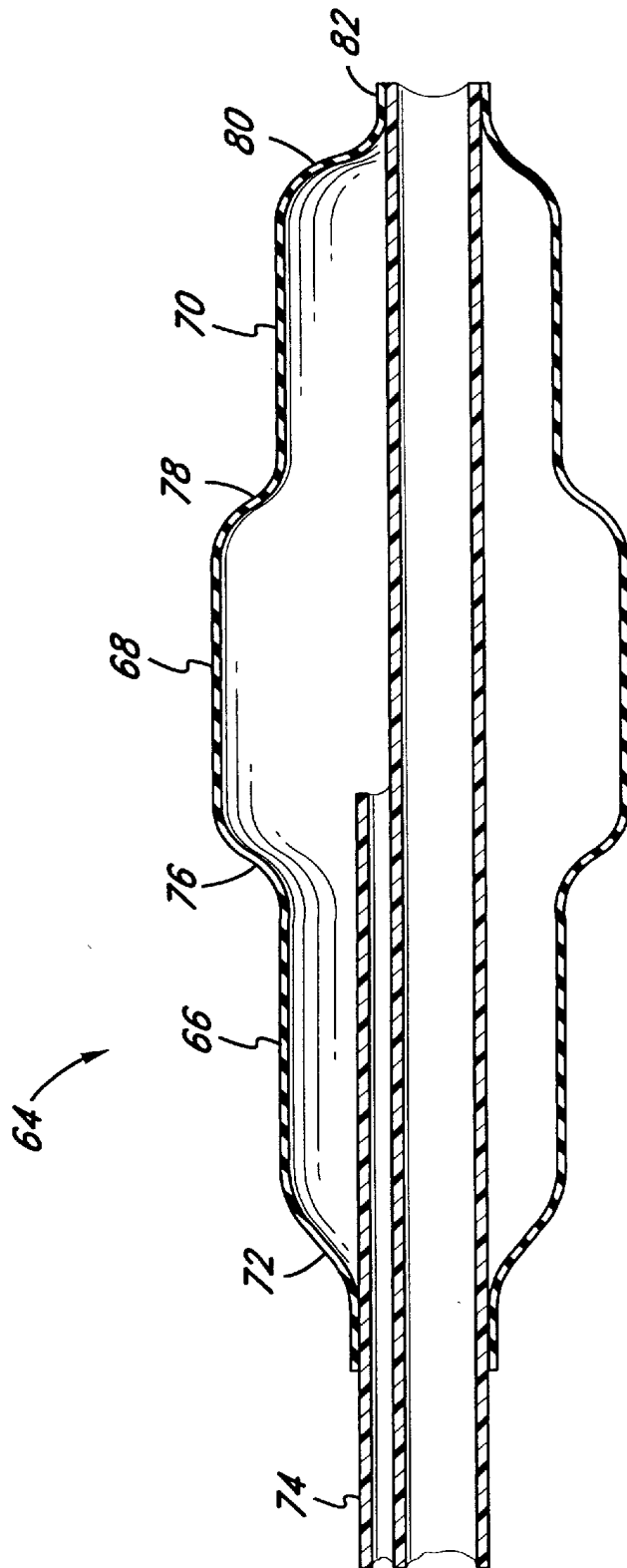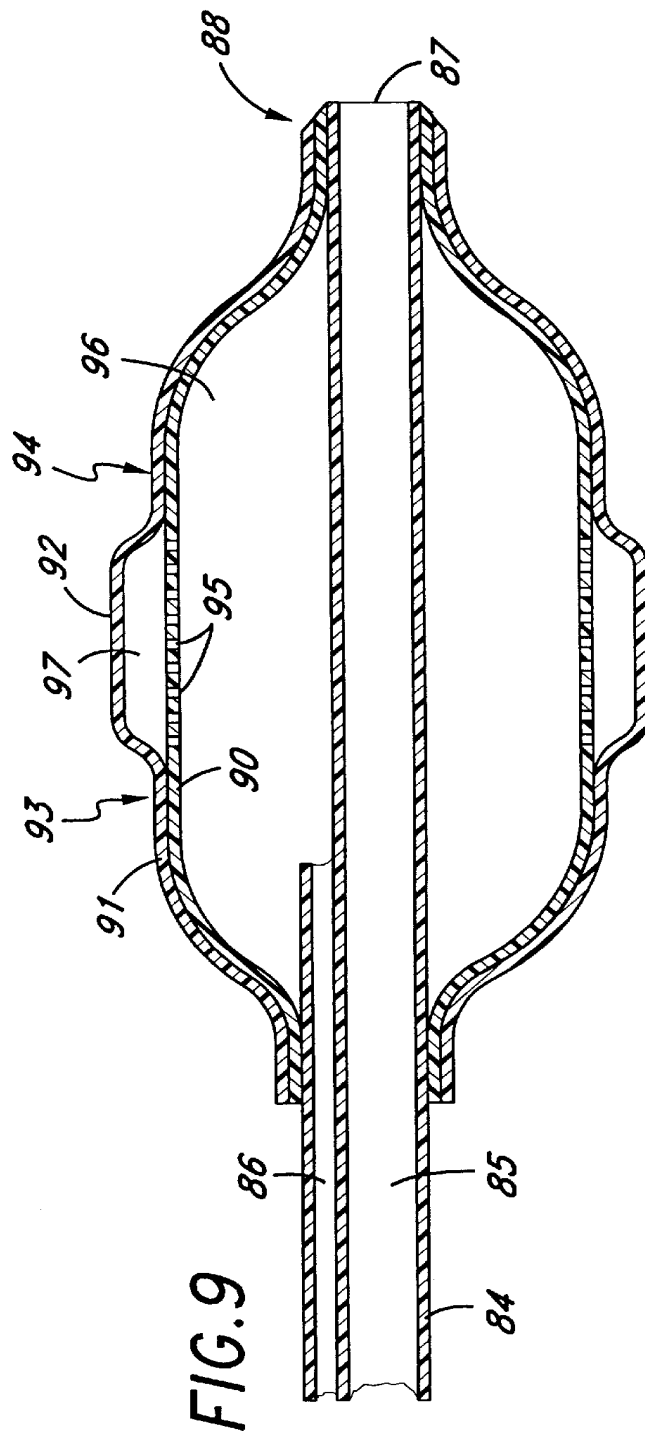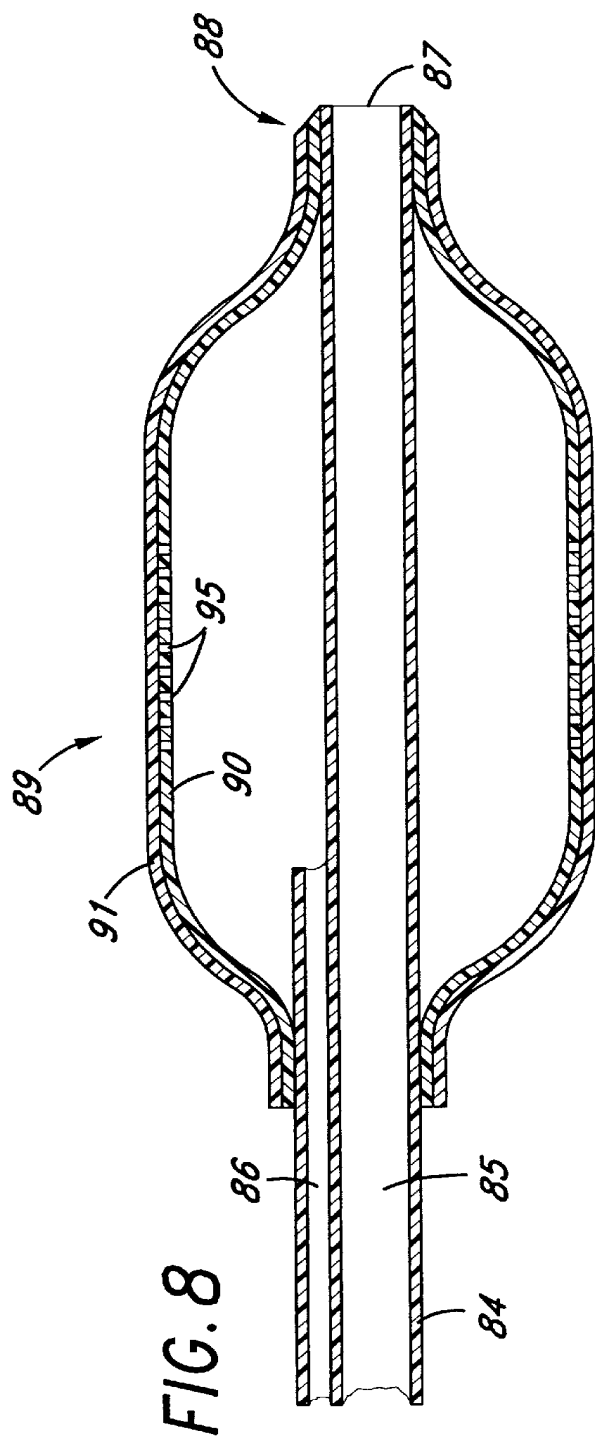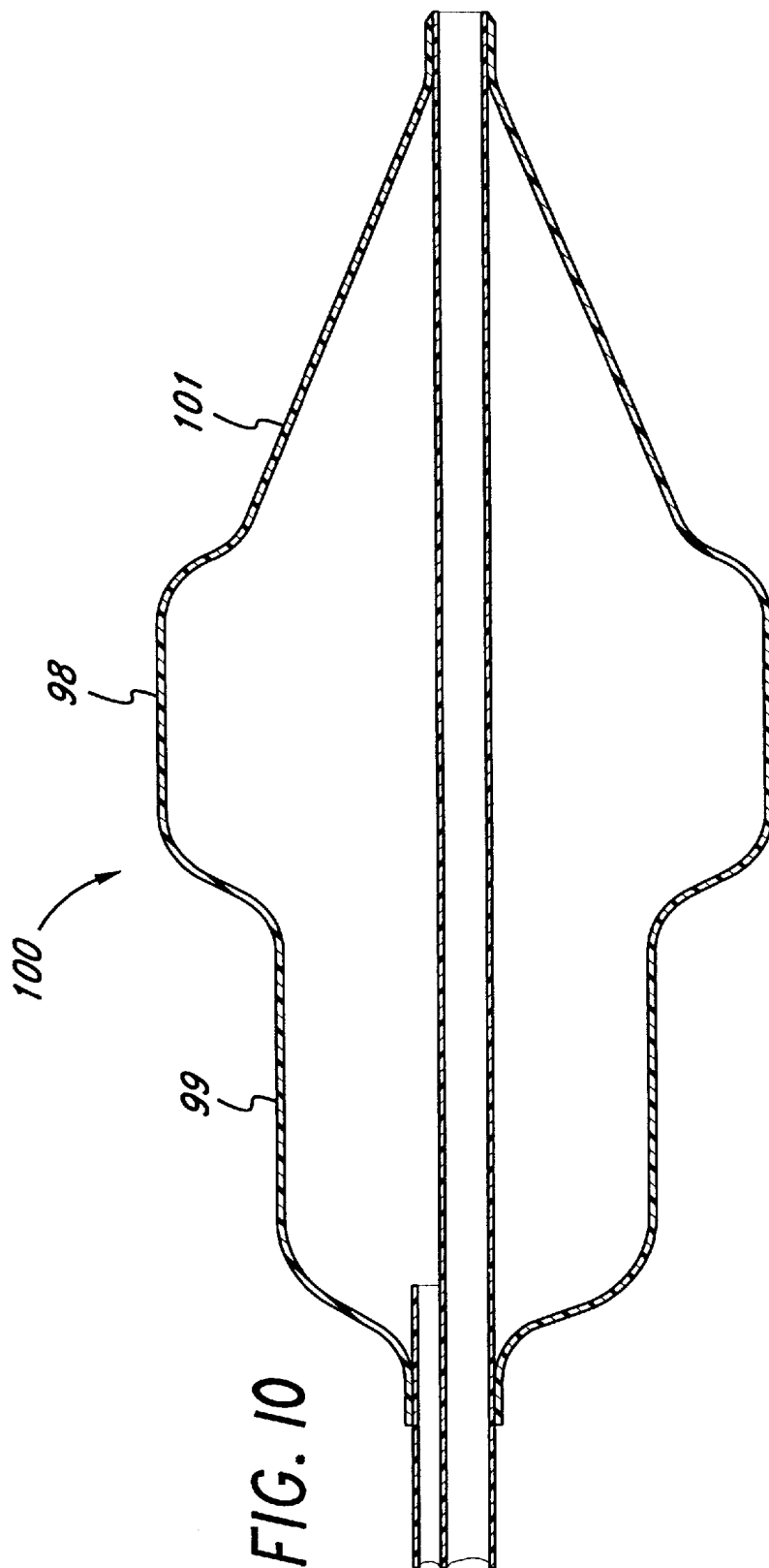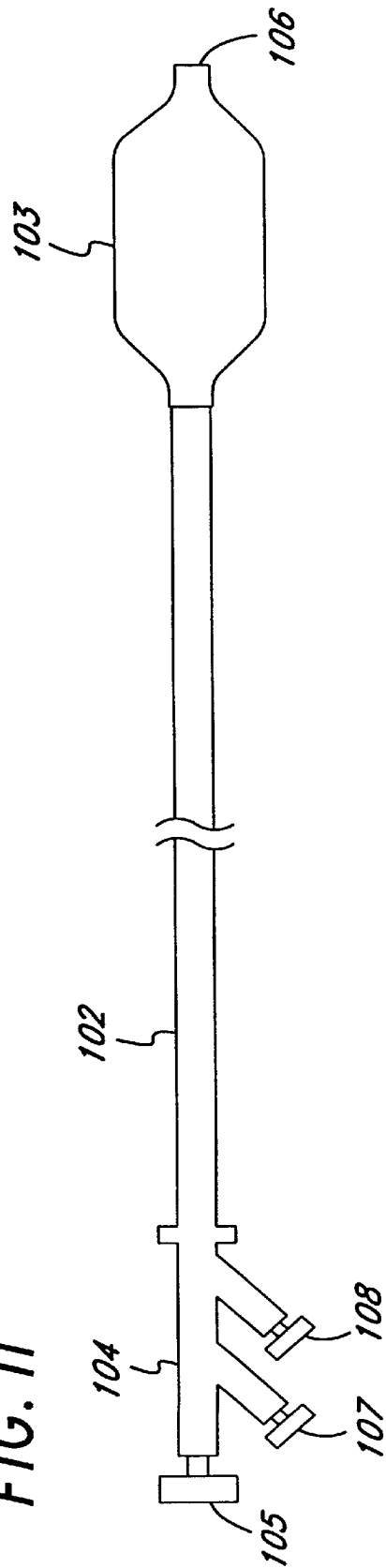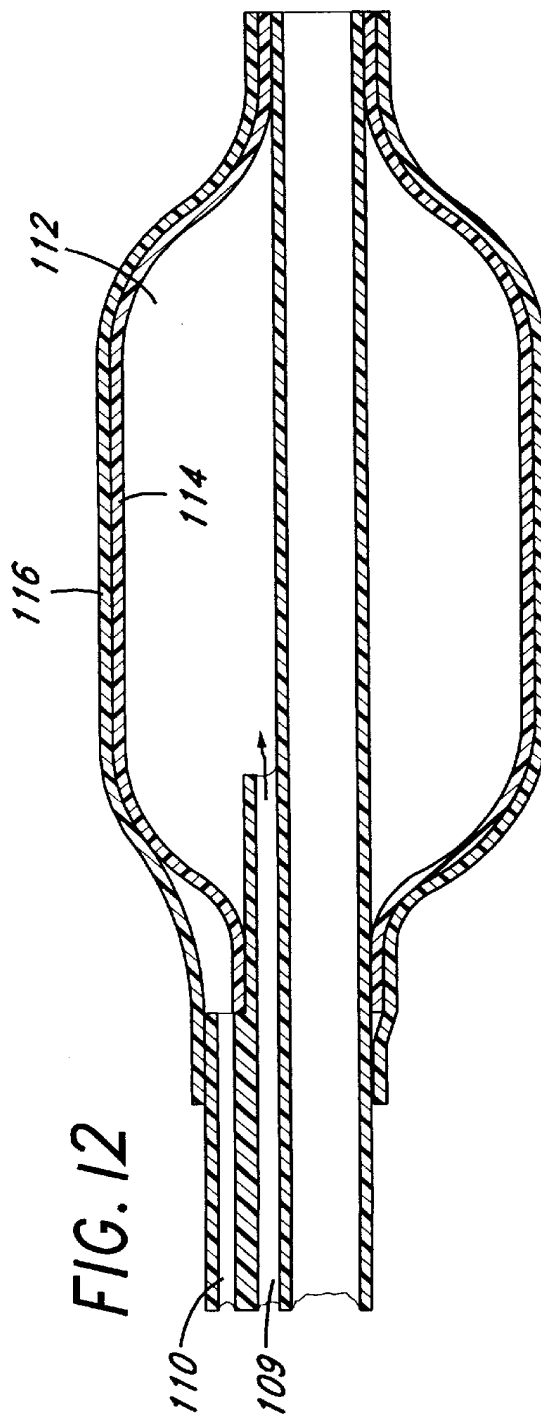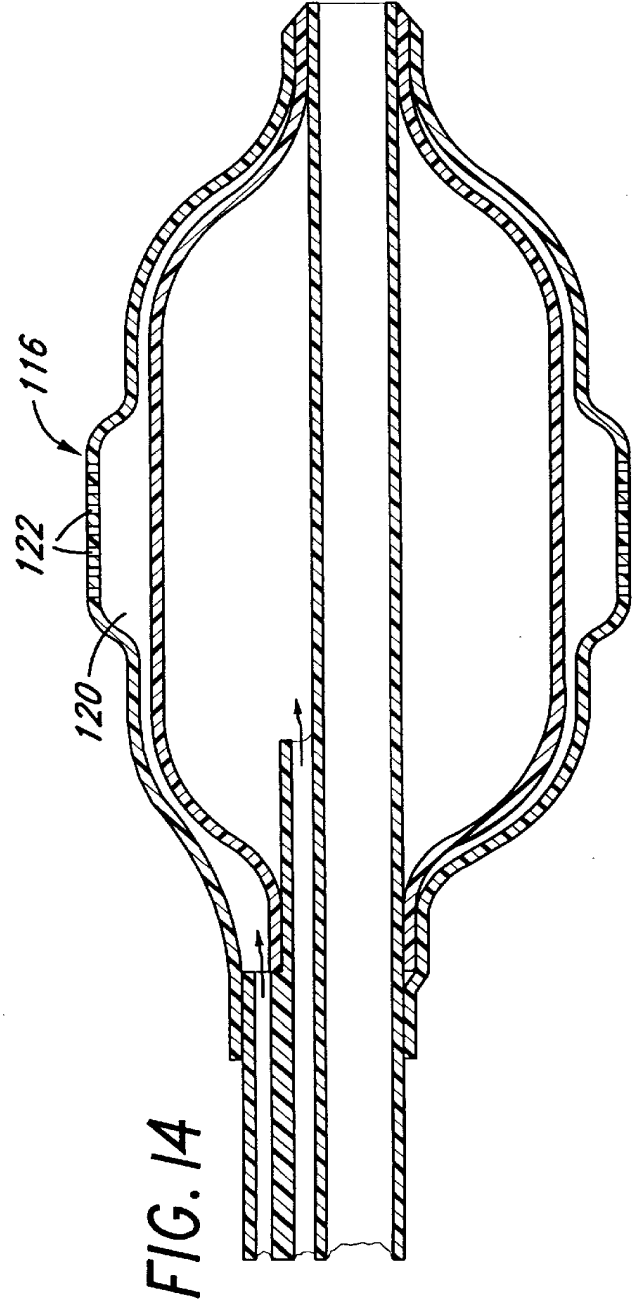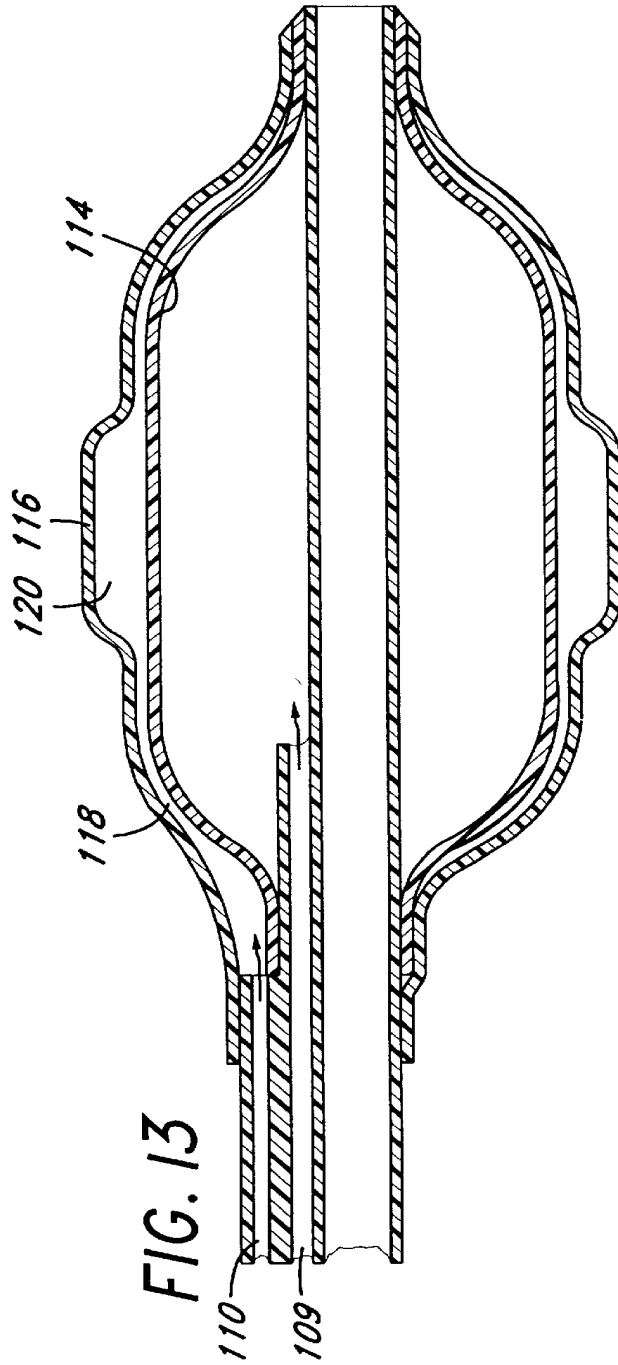
FOCALIZED INTRALUMINAL BALLOONS

The present application is a continuation-in-part of application Ser. No. 08/640,533, filed May 21, 1996 now U.S. Pat. No. 5,645,560 which is a continuation-in-part of copending application Ser. No. 08/670,683 filed Jun. 26, 1996, the disclosures of which are hereby incorporated herein by reference.

BACKGROUND OF THE INVENTION

The present invention relates to catheters for insertion into a body lumen. More particularly, the present invention relates to "focal" balloon dilatation catheters for use in the vascular system. As used herein, "focal" balloons are balloons which focus or concentrate expansive energy at one or more predetermined regions along the surface of the balloon.

Prior art vascular dilatation balloons on typical dilatation catheters tend to fall into one of two broad classes. Most are considered noncompliant balloons, formed from a generally nondistensible material such as polyethylene. The perceived advantage of the noncompliant balloons is that they exhibit a substantially uniform exterior inflated profile which remains substantially unchanged upon incremental increases in inflation pressure. In theory, noncompliant balloons are advantageous because they allow the introduction of increased inflation pressure to break particularly calcified lesions, yet retain a predictable inflated profile so that damage to the surrounding native lumen is minimized.

Certain compliant balloons are also known in the art. A compliant balloon is one which is able to grow in diameter in response to increased inflation pressure. One difficulty with compliant balloons, however, is that inflation within a difficult lesion can cause the balloon to inflate around the plaque to produce a generally hourglass-shaped inflated profile. This can result in damage to the native vessel adjacent the obstruction, while at the same time failing to sufficiently alleviate the stenosis.

In use, both the compliant and noncompliant balloons are generally inflated within a vascular stenosis to a rated inflation pressure. At that pressure, the configuration of most balloons in an unrestricted expansion is cylindrical. The balloon may be subsequently inflated to a higher inflation pressure if that is desirable in the clinician's judgment. However, the clinician has no effective way to assess the actual inflated diameter of the balloon in vivo based upon the unconstrained in vitro balloon specifications. The in vivo expansion characteristics of the balloon may track or deviate from the in vitro specifications depending upon the morphology of the lesion and the appropriateness of the selected balloon size. The clinician may know only generally or not at all the degree of calcification of the lesion, the symmetry or asymmetry, whether the lesion is soft or resilient, or other variations which affect inflation. In applications where a relatively accurate inflated diameter is desired, such as in certain dilatations or in the implantation of tubular stents, the clinician using prior dilatation balloons thus may n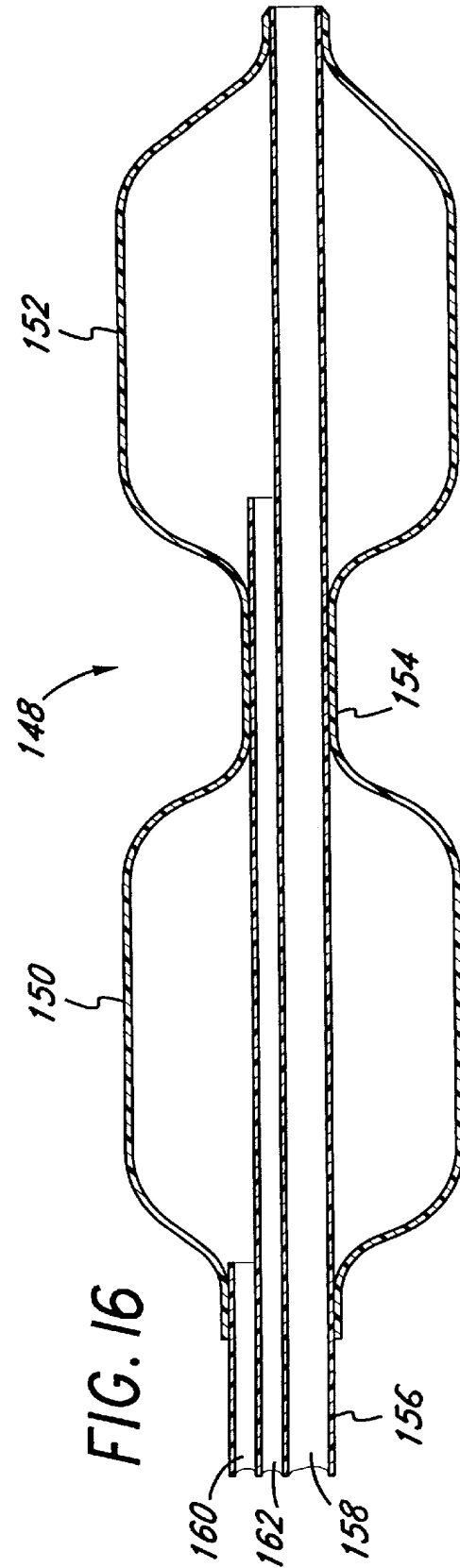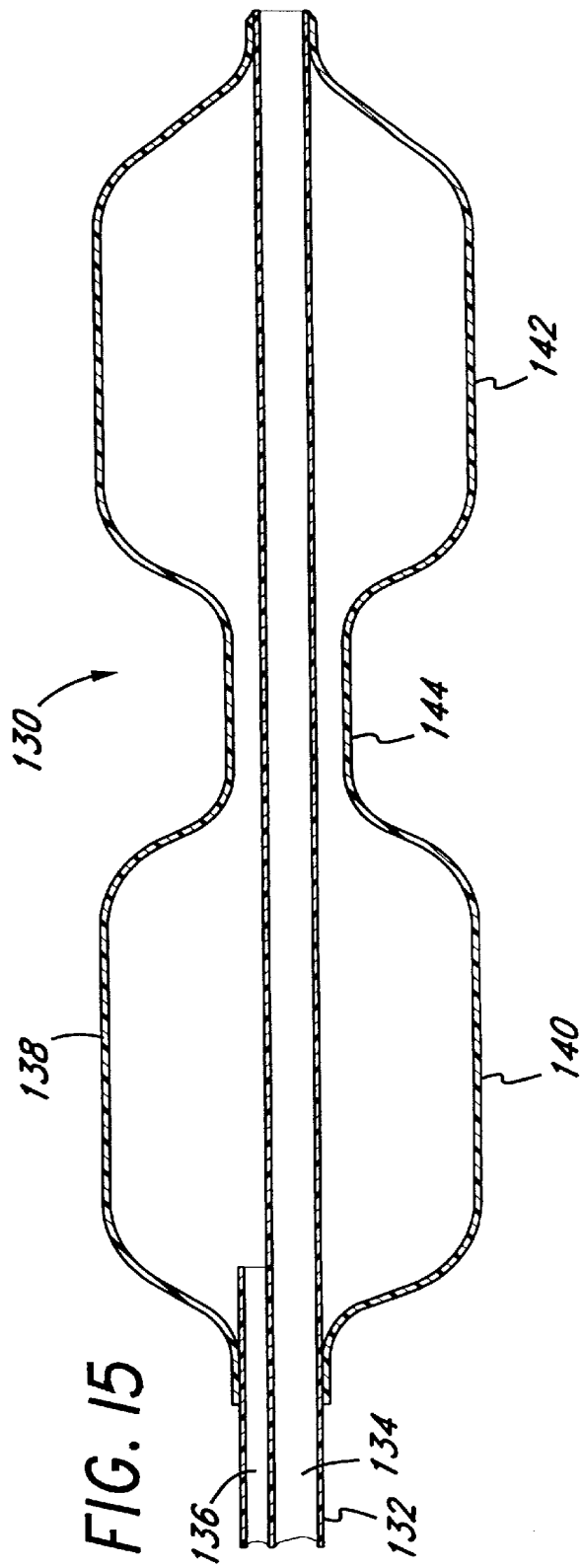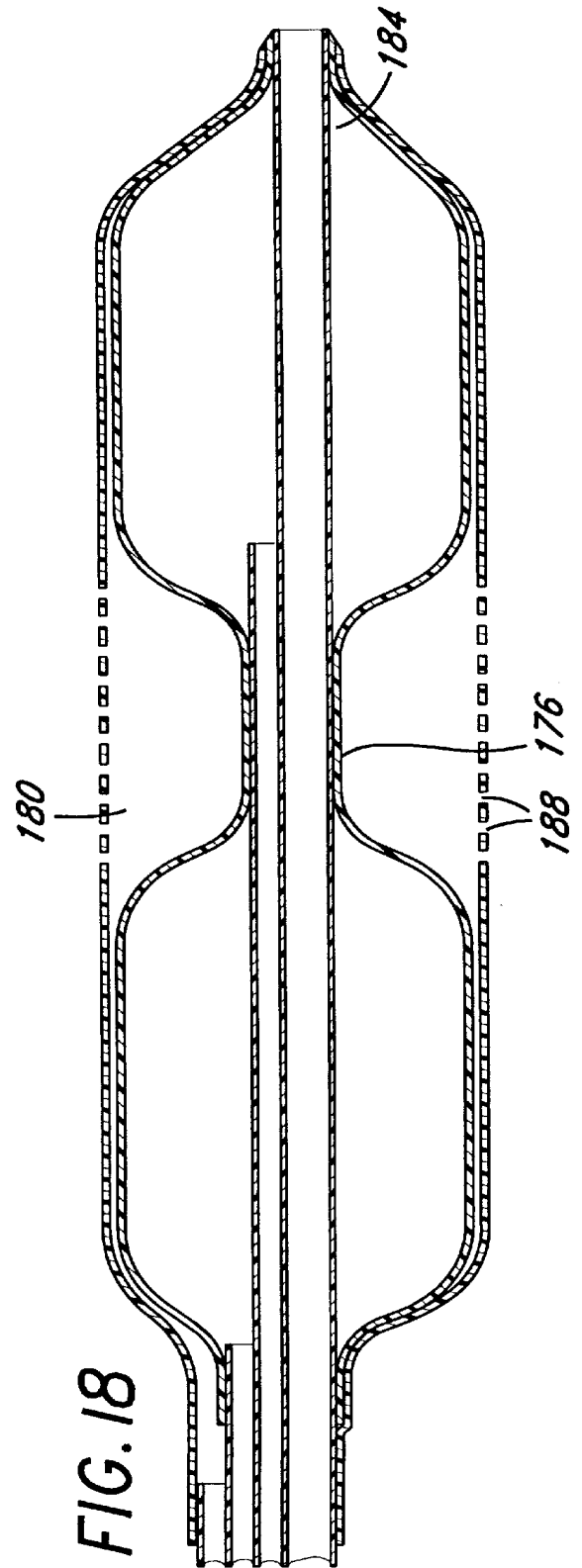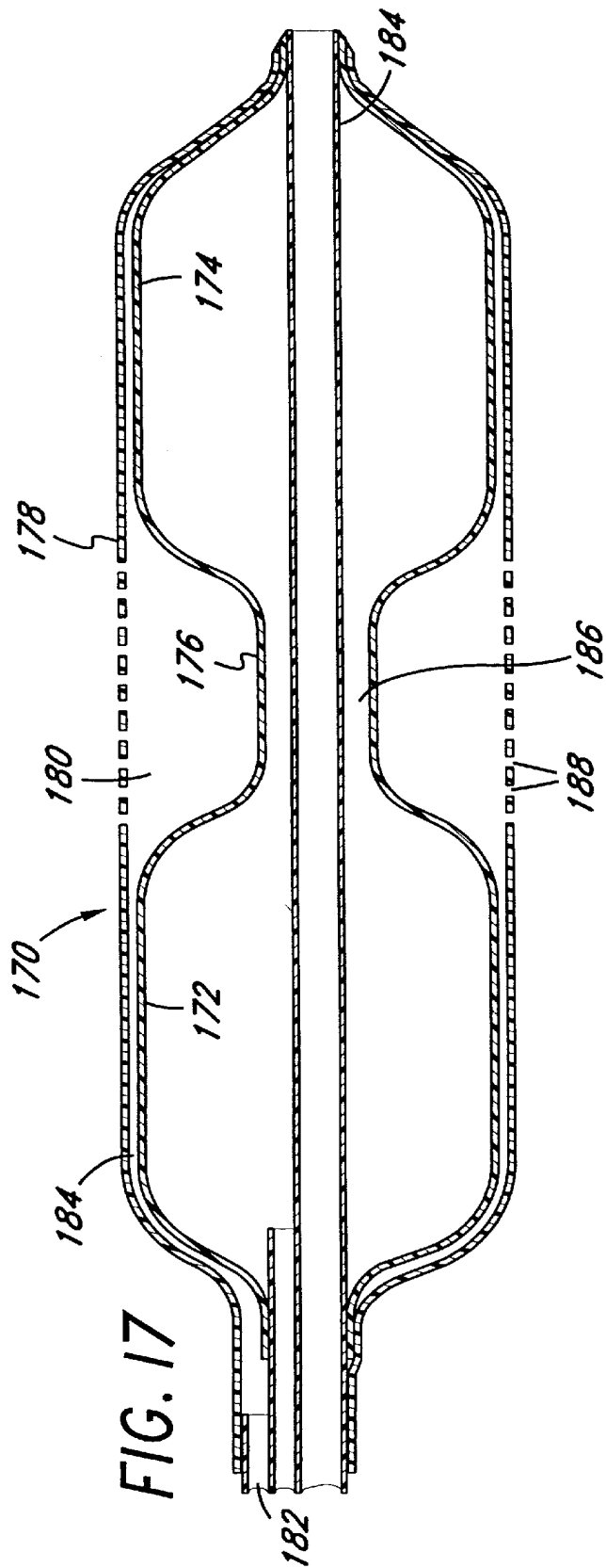ot have enough information about the dilatation characteristics of a particular lesion to optimize the dilatation or stent implantation procedure.

Therefore, there exists a need in the art for a vascular dilatation catheter with a balloon which is able to grow predictably in response to increased inflation pressure, and the expansion of which the clinician can observe in real time in comparison to a known diameter reference.

SUMMARY OF THE INVENTION

There is provided in accordance with one aspect of the present invention a balloon catheter comprising an elongate

flexible tubular body and an inflatable balloon on the tubular body. A proximal segment, a central segment and a distal segment on the balloon are inflatable to a first inflated diameter at a first inflation pressure, and the proximal and distal segment expand to a second, greater inflated diameter at a second greater inflation pressure. The central segment of the balloon remains at a diameter which is less than the second diameter, at the second inflation pressure. In one embodiment, the balloon additionally comprises at least one expansion limiting band on the central segment to limit inflation of the central segment of the balloon. Preferably, the expansion limiting band limits expansion of the central segment to no more than about the first inflated diameter.

In accordance with another aspect of the present invention, there is provided a method of treating a site in a body lumen. The method comprises the steps of providing a catheter of the type having an elongate flexible tubular body and a dilatation balloon on the body. A proximal segment, a distal segment and a central segment of the balloon are inflatable to a first diameter at a first inflation pressure, and the proximal and distal segments of the balloon are inflatable to a second, greater diameter, at a second, greater inflation pressure. The central segment remains substantially at the first diameter at said second inflation pressure.

The catheter is positioned within a body lumen so that the balloon is adjacent a treatment site, and the balloon is inflated to the first inflation pressure. At the first inflation pressure, the proximal segment, the distal segment and the central segment are inflated to no more than about the first inflation diameter. The balloon is thereafter inflated to a second inflation pressure so that the proximal and distal segments are expanded to the second inflation diameter, while the central segment is simultaneously restrained against further material radial expansion.

Optionally, the foregoing method comprises the additional step of expressing a therapeutic or diagnostic media from the central segment of the balloon to the site in the body lumen.

In accordance with a further aspect of the present invention, there is provided a method of implanting a tubular graft within a body lumen. The method comprises providing an elongate flexible tubular body having an inflatable balloon thereon, the balloon inflatable to a first diameter at a first inflation pressure to produce a generally cylindrical balloon profile, and proximal and distal portions of the balloon are additionally inflatable to a second, larger diameter at a second, greater inflation pressure. An expandable tubular graft is positioned on the balloon, and the balloon is thereafter positioned within a body lumen adjacent a treatment site.

The balloon is inflated to the first inflation diameter to expand the tubular graft and thereafter inflation pressure is increased to the second inflation pressure such that the proximal and distal portions of the balloon inflate to the second, larger diameter, to further expand the proximal and distal portions of the tubular graft.

Further features and advantages of the present invention will become apparent to one of skill in the art in view of the Detailed Description of Preferred Embodiments which follows, when considered together with the attached drawings and claims.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view of a preferred embodiment of a variable diameter inflation catheter of one aspect of the present invention, in the second inflation configuration.

FIG. **2** is a partial cross-sectional view of a preferred embodiment of the variable diameter inflation catheter at a first inflation profile.

FIG. **3** is a partial cross-sectional view of a preferred embodiment of the variable diameter inflation catheter at a second inflation profile.

FIG. **4** is a schematic view of the embodiment of FIG. **1**, shown in the first inflation configuration.

FIG. **5** illustrates a comparison of compliance curves between the reference zones and the focal zone as a function of increased inflation pressure in a differential compliance focal balloon of the present invention.

FIG. **6** is a schematic illustration of a balloon of the present invention having a relatively thin wall in the focal section.

FIG. **7** is a cross sectional schematic illustration of a fixed focal balloon catheter of the present invention.

FIG. **8** is a cross sectional view through a dual layer balloon having a central compliant zone thereon.

FIG. **9** is a cross sectional view as in FIG. **8**, with the compliant zone in the expanded configuration.

FIG. **10** is a cross sectional schematic view of a balloon profile having a focal zone and a tapered distal zone.

FIG. **11** is a schematic elevational view of a dual inflation lumen catheter.

FIG. **12** is a cross sectional view through a dual layer balloon having a unique inflation lumen for each layer.

FIG. **13** is a cross sectional view of a dual layer balloon as in FIG. **12**, in the focalized configuration.

FIG. **14** is a cross sectional view through a balloon similar to that in FIG. **13**, but with added delivery capability.

FIG. **15** is a cross sectional schematic illustration of a balloon having a proximal and a distal lobe.

FIG. **16** is a cross sectional schematic illustration of a dual balloon configuration.

FIG. **17** is a cross sectional illustration of a dual lobed balloon adapted for delivery of media into the vessel.

FIG. **18** is a cross sectional view of a dual balloon catheter, configured for delivery of media into the vessel.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIG. **1**, there is disclosed a variable diameter inflation catheter **10** in accordance with of one aspect of the present invention. Catheters embodying additional features known in the vascular dilatation art, such as implantable stents, drug delivery, perfusion and dilatation features, or any combination of these features, can be used in combination with the focal balloon of the present invention as will be readily apparent to one of skill in the art in view of the disclosure herein.

The catheter **10** generally comprises an elongate tubular body **12** extending between a proximal control end **14** and a distal functional end **16**. The length of the tubular body **12** depends upon the desired application. For example, lengths in the area of about 120 cm to about 140 cm are typical for use in percutaneous transluminal coronary angioplasty applications.

The tubular body **12** may be produced in accordance with any of a variety of known techniques for manufacturing balloon-tipped catheter bodies, such as by extrusion of appropriate biocompatible plastic materials. Alternatively, at least a portion or all of the length of tubular body **12** may

comprise a spring coil, solid walled hypodermic needle tubing, or braided reinforced wall, as is understood in the catheter and guide wire arts.

In general, tubular body **12**, in accordance with the present invention, is provided with a generally circular cross-sectional configuration having an external diameter within the range of from about 0.03 inches to about 0.065 inches. In accordance with one preferred embodiment of the invention, the tubular body **12** has an external diameter of about 0.042 inches (3.2 f) throughout most of its length. Alternatively, generally triangular or oval cross-sectional configurations can also be used, as well as other non-circular configurations, depending upon the number of lumen extending through the catheter, the method of manufacture and the intended use.

In a catheter intended for peripheral vascular applications, the tubular body **12** will typically have an outside diameter within the range of from about 0.039 inches to about 0.065 inches. In coronary vascular applications, the tubular body **12** will typically have an outside diameter within the range of from about 0.026 inches to about 0.045 inches. Diameters outside of the preferred ranges may also be used, provided that the functional consequences of the diameter are acceptable for the intended purpose of the catheter. For example, the lower limit of the diameter for tubular body **12** in a given application will be a function of the number of fluid or other functional lumen, support structures and the like contained in the catheter, and the desired structural integrity.

Tubular body **12** must have sufficient structural integrity (e.g., "pushability") to permit the catheter to be advanced to distal arterial locations without buckling or undesirable bending of the tubular body **12**. The ability of the body **12** to transmit torque may also be desirable, such as in embodiments having a drug delivery capability on less than the entire circumference of the delivery balloon. Larger diameters generally have sufficient internal flow properties and structural integrity, but reduce perfusion in the artery in which the catheter is placed. Increased diameter catheter bodies also tend to exhibit reduced flexibility, which can be disadvantageous in applications requiring placement of the distal end of the catheter in a remote vascular location. In addition, lesions requiring treatment are sometimes located in particularly small diameter arteries, necessitating the lowest possible profile.

As illustrated schematically in FIG. **1**, the distal end **16** of catheter **10** is provided with at least one inflation balloon **18** having a variable diameter. The proximal end **14** of catheter **10** is provided with a manifold **20** having a plurality of access ports, as is known in the art. Generally, manifold **20** is provided with a guide wire port **22** in an over the wire embodiment and a balloon inflation port **24**. Additional access ports are provided as needed, depending upon the functional capabilities of the catheter **10**. The balloon **18** can also be mounted on a rapid exchange type catheter, in which the proximal guidewire port **22** would be unnecessary as is understood in the art. In a rapid exchange embodiment, the proximal guidewire access port is positioned along the length of the tubular body **12**, such as between about 4 and about 20 cm from the distal end of the catheter.

Referring to FIGS. **2** and **3**, the two-step inflation profile of the inflation balloon **18** is illustrated. In FIG. **2**, the balloon **18** is illustrated at a first inflation profile, in which in an unconstrained expansion it exhibits a substantially cylindrical central working profile. The dimensions in FIG. **2** are exaggerated to illustrate a proximal segment **26** and a distal segment **28** which are axially separated by a central

focal segment **30**. However, as will be understood by one of ordinary skill in the art, when the balloon **18** is inflated to the first inflation profile, the exterior of the balloon **18** preferably exhibits a substantially smooth cylindrical working profile.

In FIG. **3**, the inflation balloon **18** is illustrated at a second inflation profile. The proximal segment **26** and the distal segment **28** of the balloon are separated by the central focal segment **30** having a greater diameter. The configuration of FIG. **2** is achieved by inflating the balloon **18** to a first inflation pressure, while the configuration of FIG. **3** is achieved by increasing the inflation pressure to a second, higher pressure as will be discussed below.

The details of one preferred embodiment of the variable diameter inflation catheter **10** are discussed with reference to FIGS. **2** and **3**. Preferably, the tubular body **12** is provided with at least a guidewire lumen **32** extending all the way through the balloon **18**, and an inflation lumen **34** extending into the proximal end of the balloon **18**.

In the illustrated embodiment, an inner balloon **36** is disposed coaxially within an outer balloon **38**. A substantially nondistensible expansion limiting band **40** is disposed in between the balloons **36** and **38** adjacent a proximal annular shoulder **42**, to limit the radial expansion of the balloon **18**. Similarly, a distal expansion limiting band **44** is disposed between the inner balloon **36** and outer balloon **38** adjacent a distal annular shoulder **46**.

Expansion limiting bands **40** and **44** or other inflation limiting structures can be provided in any of a variety of ways which will be well-understood by one of skill in the art in view of the disclosure herein. For example, in one embodiment, the bands **40** and **44** each comprise a tubular section of polyester, each having an axial length of about 5 mm, a diameter of about 2.5 mm and a wall thickness of about 0.0003 inches. Other generally nondistensible materials such as nylon, polyamide, Kevlar fiber, cross-linked polyethylene, polyethylene terephthalate and others, may be utilized to accomplish the expansion-limiting effect.

The expansion limiting characteristics can be achieved by the addition of a structure that is discrete from the balloon, or by modifying the expansion properties of the balloon material itself. For example, the balloon can be provided with zones of differing wall thickness, or zones having different levels of cross linking as will be discussed.

In general, the bands **40** and **44** must be of a sufficient thickness or structural integrity for the particular material used to substantially withstand inflation under the pressures normally utilized in the context of dilatation catheters. However, the bands **40** and **44** are preferably thin enough to provide a substantially smooth exterior surface of the balloon **18**.

Preferably, as illustrated in FIGS. **2** and **3**, the expansion-limiting bands **40** and **44** are sandwiched between the inner balloon **36** and the outer balloon **38**. In alternative embodiments, the expansion-limiting bands **40** and **44** or other inflation limiting structures may be coated or mounted on the exterior surface of the balloon **18**, the interior surface of the balloon **18** or within the wall of the balloon **18**. Balloon **18** can be provided with two or more layers as illustrated, or with only a single layer as will be discussed.

The axial length of the bands **40** and **44** can be varied widely depending upon the dimensions and the objectives of the catheter **10** as will be apparent to one of ordinary skill in the art. Further, the proximal band **40** and distal band **44** need not be of similar lengths. In general, however, some examples of dimensions which are useful in the coronary

angioplasty dilatation environment are reproduced in Table 1 below, in which A represents the axial length of the balloon **18** between proximal shoulder **42** and distal shoulder **46**, B represents the axial distance between distal shoulder **46** and transition point **48**, and C represents the axial length of the central focal segment **30**. The dimensions of Table 1 are exemplary only, and the present invention can be accomplished using a wide variety of other dimensions as will be apparent to one of skill in the art.

TABLE 1

A	B	C
20 mm	5 mm	10 mm
30 mm	5 mm	20 mm
40 mm	5–10 mm	20–30 mm

The catheter **10** illustrated in FIGS. **2** and **3** can be manufactured in accordance with any of a variety of techniques which will be appreciated by one of ordinary skill in the art in view of the disclosure herein. In the following disclosure, particular materials and dimensions will be used as an example only, and other dimensions and materials can be selected depending upon the desired characteristics of the finished product.

In one particular method of manufacturing, a low density polyethylene extrusion stock tube having an inside diameter of about 0.018 inches and an outside diameter of about 0.043 inches is used for the inner and outer balloons **36**, **38**.

The polyethylene stock tubing is cross-linked by exposure to an electron beam in accordance with techniques well known in the art. A test segment of the cross-linked stock tubing is free blown up to 3.0 mm in diameter. If the cross-linked stock tubing can be free blown to a diameter greater then 3.0 mm, the stock tubing is cross-linked again and retested until the desired free blow diameter is achieved.

The appropriately cross-linked stock tubing is then blown to a diameter of 2.5 mm within a teflon capture tube (not shown) which acts to mold the balloon to its desired first inflation diameter. The teflon capture tube is a generally tubular body which has approximately the same inside diameter as the desired inflation diameter of the balloon. The teflon capture tube is heated by any of a number of heating means such as electric coils or a furnace to a temperature which is sufficient to mold the balloon to the desired inflation diameter. In this case, the cross-linked polyethylene balloon is preferably heated to a temperature of about 300° F. The teflon chamber is then cooled to a temperature below the softening temperature of the balloon. Once cooled, the balloon is deflated and removed from the capture tube.

A section of inflation balloon material is thereafter stretched with application of heat to neck down the proximal and distal ends **37**, **39** to a thickness of about 0.001 inches and a diameter which relatively closely fits the portion of the tubular catheter body **12** to which it is to be sealed.

The balloon is then attached to the tubular body **12** by any of a variety of bonding techniques known to one of skill in the art such as solvent bonding, thermal adhesive bonding or by heat shrinking/sealing. The choice of bonding techniques is dependent on the type of balloon material and tubular body material used to form the catheter **10**.

In one particular method of manufacture, inner balloon **36** and outer balloon **38** are attached to the catheter body **10**. The proximal necked end **37** of the inner balloon **36** is heat sealed around the catheter body **12**. The distal necked end **39** of the inner balloon **36** is thereafter heat sealed around the

distal end 16 of the catheter body 12. In general, the length of the proximal end 37 and the distal end 39 of the inner balloon 36 which is secured to the catheter body 12 is within the range of from about 3 mm to about 10 mm, however the proximal and distal balloon necked ends 37, 39 are as long as necessary to accomplish their functions as a proximal and distal seal.

Expansion limiting bands 40 and 44 are respectively positioned at the proximal segment 26 and the distal segment 28 of the inner balloon 36 and may be bonded or otherwise secured to the inner balloon 36. The outer balloon 38 is thereafter be mounted to the catheter body 12 in a similar manner as the inner balloon 36, following "necking down" of the proximal and distal axial ends of the outer balloon 38 by axial stretching under the application of heat. The outer balloon 38 is advanced axially over the inner balloon 36 and the expansion limiting bands 40 and 44. The outer balloon 38 may thereafter be bonded to the inner balloon 36, and to the expansion limiting bands 40 and 44 by any of a variety of bonding techniques such as solvent bonding, thermal adhesive bonding or by heat sealing also depending on the type of balloon material used. Alternatively, the expansion limiting bands are simply entrapped between the balloons without any bonding or adhesion.

In a preferred embodiment, the inner balloon and the outer balloon 36, 38 are both cross-linked polyethylene balloons which are difficult to bond together using conventional solvents. If sealing is desired, the inner balloon 38 and the outer balloon 38 are heat sealed together as described below. In another embodiment, the inner balloon 36 and outer balloon 38 are secured together through the use of a UV-curable adhesive.

The inner balloon 36 and the outer balloon 38, once mounted to the catheter body 12, can be heat sealed together in a heating chamber (not shown) such as a Teflon capture tube. Inner balloon 36 and outer balloon 38 are inflated in the chamber until the inner balloon and the outer balloon inflate to the first inflation diameter. The heating chamber is heated by any of a number of heating means such as electric coils or a furnace to heat air to a temperature which is sufficient to bond the two balloons 36, 38 together. In this case, the cross-linked polyethylene balloons are preferably heated to a temperature of about 300° F. within the chamber which causes both balloons 36, 38 to seal together to form a double walled variable diameter inflation balloon 18. The chamber is then cooled to a temperature below the softening temperature of the inner and outer balloons 36 and 38. Once cooled, the variable diameter balloon 18 is deflated and the catheter 10 is removed from the chamber.

It will be apparent to one of skill in the art, that it is possible to attach the inner balloon 36 and the outer balloon 38 to the catheter body 12 without adhesively bonding or otherwise securing the two balloons together. In this case, the two balloons will respond to the applied inflation pressure with the inner balloon 36 forcing the outer balloon 38 to simultaneously inflate both balloons 36, 38. The expansion limiting bands 40 and 44 can be merely sandwiched between the inner balloon 36 and the outer balloon 38 and do not in this embodiment need to be bonded to either balloon.

The variable diameter balloon design of the present invention can also be accomplished with a single layer balloon or a double layer balloon without the inclusion of additional expansion limiting bands. This is accomplished by decreasing the relative compliance of the zones of the

balloon that are intended to remain at the first inflated diameter. Alternatively, the compliance of the focal section can be increased relative to that of the reference zones.

For example, polyethylene extrusion stock is cross-linked to 3.0 mm and blown into a mold of a diameter of about 2.5 mm as described above to form a balloon. Balloon stock can be crosslinked either before or after mounting on the catheter, and in either the inflated or deflated state. The proximal and distal segments 26, 28 of the balloon on the catheter 10 are masked such as with steel clamps or other masks known in the art to block electron beam penetration, leaving the central segment 30 of the balloon exposed. The central segment 30 of the balloon 18 is exposed again to an electron beam source to be further cross-linked at the 2.5 mm diameter. Balloons manufactured in this manner have been found to exhibit a relatively highly compliant central zone and relatively less complaint axial end zones in a manner that achieves the two-step dilatation as illustrated in FIGS. 2 and 3.

Single layer balloons having the differential compliancy characteristics described above can also be provided using other balloon materials such as polyethylene terephthalate (PET). For example, a one piece single layer PET balloon can be provided with a thinner wall in the focal section compared to the one or two reference sections of the balloon. FIG. 6 discloses a schematic illustration of a balloon 50 in accordance with this aspect of the present invention. The balloon 50 defines an interior space 51 for containing inflation media as is understood in the art. The balloon 50 generally comprises a distal neck portion 52 and proximal neck portion 54 for securing the balloon 50 to the catheter. A working length of the balloon 56 extends between proximal shoulder 55 and distal shoulder 57.

The working length 56 of the balloon 50 is provided with a proximal reference zone 62 and a distal reference zone 58, separated by a focal zone 60. As has been discussed in connection with previous embodiments, the balloon 50 can alternately be provided with only a single reference zone either 58 or 62, together with the focal zone 60. Preferably, however, both proximal and distal reference zones 62 and 58 will be utilized with a central focal zone 60.

The thickness of at least a portion of the balloon wall in the area of focal zone 60 is thinner than the wall thickness in the reference zones 62 and 58.

In one embodiment of the single wall focal balloon of the present invention, the balloon comprises PET. The balloon has a working length of about 20 mm, and the proximal and distal reference zones 62 and 58 each have a length of about 5 mm. The focal zone 60 has a length of about 10 mm. The first inflated diameter at 8 ATM is about 3.0 mm, and the focal section inflates in vitro to about 3.5 mm at 16 ATM. The wall thickness in the area of reference zones 62 and 58 is about 0.001 inches, and the wall thickness in the area of focal zone 60 is about 0.0007 inches.

Whether the balloon comprises PET or other balloon materials known in the art, a thinner focal section compared to the thickness at the reference section can be provided using a variety of techniques. For example, the PET balloon can be exposed to heat and stretched in the center portion to provide a relatively thinner wall than the end reference portions. Alternatively, the balloon can be heated at its ends to shrink the balloon thereby increasing the thickness of the material in the regions exposed to heat.

Thinning a portion of the wall of the balloon by stretching the material can be accomplished in any of a variety of ways that will be apparent to those of skill in the art, in view of

the disclosure herein. One method of reducing the wall thickness in the region of the focal zone involves an axial elongation of the tubular balloon stock under the application of heat. In general, the present inventor has found that the percent reduction in wall thickness is roughly equivalent to the percent axial elongation of the tubular stock. Thus, the tube stock is axially elongated a sufficient distance to achieve the desired reduction in wall thickness.

In one application of the invention, a molded PET balloon having a wall thickness of about 0.001 inches was axially elongated a sufficient distance to reduce the focal zone thickness to about 0.0007 inches. A molded PET balloon having a wall thickness of about 0.0008 inches was axially elongated by 40% to produce a wall thickness of about 0.0005 inches.

In one application of the method of the invention, a length of tubular polymeric stock is provided. The stock may be cut to a useful working length, such as 10–20 centimeters. Excess stock length following the elongation process will be trimmed prior to mounting of the balloon on the catheter shaft as will be understood by those of skill in the art.

A 15 cm length of PET balloon tubing having a wall thickness of about 0.0010 inches and an inflated outside diameter of about 3.0 mm was clamped at or near each end in a device configured to apply an axially stretching force to the tubing. Prior to closing one of the clamps, a needle was advanced through the open end of the tubing so that the tubing can be pressurized following clamping. Following clamping, the tubing was inflated under a pressure of about 100 psi, and axial tension in the area of about 1 lb. was applied.

The foregoing setup for a 3 mm balloon was accomplished inside of a 3 mm capture tube. First and second aluminum heat sinks were thermally coupled to the capture tube, and spaced about 5 mm apart. A hot air heater having a length of about 5 mm in the axial tube direction was positioned in between the heat sinks and advanced towards the capture tube to heat the capture tube. The heat sinks assist in localizing the region of the tubing stock which will be heated by the heater, as will be understood by those of skill in the art.

Upon reaching a temperature of about 200° F., the tube stock begins to stretch under the axial tension. The axial length of travel of the stretching clamps is preferably limited to provide a predetermined limit for the percentage axial elongation. In one application of the invention, the 5 mm heated section grew to about 5 or 7 mm in axial length following a 20%–40% increase in the distance between the clamps. Any of a variety of modification to the foregoing procedure can be readily envisioned by those of skill in the art. For example, alternate sources of heat such as forced air heating, infra red, electrical coil, and others known in the art can be used. In addition, stretching can be accomplished through any of a variety of physical setups, which can be readily assembled by those of skill in the art. Stretching without the application of heat, such as by cold rolling or cold forming a portion of tubular stock may also provide an acceptable thinning of the balloon wall for certain types of balloon materials.

Subject to the pressure retention characteristics of bonds between dissimilar balloon materials, the balloon can alternatively be provided with a relatively more compliant material in a focal section, and a relatively less compliant material in a reference section. Balloons having a combination of materials having different compliancies can be manufactured, for example, using two extrusion heads

which alternately drive balloon material through a single orifice. Any of a variety of material pairs may be used, such as nylons of different hardness, PET and PE, and others that can be selected by those skilled in the art. As a further alternative, the focal section can be formed from an entirely different balloon which is positioned adjacent a single reference balloon or positioned in between two reference balloons to produce a balloon having some of the characteristics of the focal balloon of the present invention.

Balloons 18 made in accordance with the design illustrated in FIGS. 2 and 3 have been found to exhibit the inflation pressure profile illustrated in Table 2.

TABLE 2

PRESSURE	CENTRAL SEGMENT DIAMETER	PROXIMAL AND DISTAL SEGMENT DIAMETER
6 atm	2.5 mm	2.5 mm
7 atm	2.6 mm	2.5 mm
8 atm	2.7 mm	2.5 mm
9 atm	2.8 mm	2.5 mm
10 atm	2.9 mm	2.6 mm
11 atm	3.0 mm	2.6 mm
12 atm	3.1 mm	2.7 mm
13 atm	3.2 mm	2.7 mm
14 atm	3.2 mm	2.7 mm

The inflation pressure profile of the variable diameter inflation balloon 18 illustrated in Table 2 provides an example of the manner in which a balloon 18 made in accordance with the foregoing method is inflated with the application of increased pressure. Initially, the central segment 30 and the proximal and distal segments 26, 28 of the balloon 18 inflate together in vitro as the pressure increases. When the pressure reaches 6 ATM, for example, the diameter of the proximal and distal segments 26, 28 and the central segment 30 of the balloon all remain at about 2.5 mm. At 11 ATM, the diameter of the central segment 30 of the balloon 18 has grown to about 3 mm while the proximal and distal segments 26, 28 remained inflated to the first diameter of approximately 2.5 mm. The diameter of the central section 30 of the balloon 18 will continue to increase at least in vitro until the burst pressure of the balloon 18 is reached. In one prototype, the burst pressure was approximately 20 ATM at normal body temperature.

Both the first inflation diameter and the second inflation diameter can also be varied depending upon the desired catheter characteristics as will be understood by one of ordinary skill in the art. In a preferred embodiment, a first inflated diameter of the catheter for coronary angioplasty applications is approximately 2.5 mm. Upon an increase of pressure, this diameter grows to a second inflated diameter of approximately 3 mm in the central focal segment 30. In general, balloons can be readily constructed having a difference between the first inflation diameter and second inflation diameter anywhere within the range of from about 0.1 mm up to 1.0 mm or more, depending upon the elastic limits of the material from which the balloon was constructed. Typically, coronary angioplasty dilatation balloons will have a first diameter within the range of from about 1.5 mm to about 4.0 mm. Typical balloons for use in peripheral vascular applications will have a first inflation diameter within the range of from about 2 mm to about 10 mm.

Dilatation balloons can readily be constructed in accordance with the present invention in which entire length of the balloon from, for example, proximal shoulder 42 to distal shoulder 46 (FIG. 2) is variable from a first inflated

diameter to a second larger inflated diameter in response to increasing pressure. Alternatively, balloons in accordance with the present invention can readily be constructed in which a proximal portion of the balloon is compliant so that it can grow in response to increased pressure, while a distal portion of the balloon has a fixed inflated diameter. This configuration may be desirable, for example, when the native vessel diameter is decreasing in the distal catheter direction. Positioning the catheter so that the compliant portion is on the proximal (larger diameter) portion of the vessel may minimize damage to the vessel wall in certain applications. Alternatively, the compliant segment can readily be positioned on the distal end of the balloon with a substantially fixed inflated diameter segment on the proximal end of the balloon.

A variable diameter balloon **18** made in accordance with the foregoing designs has been found to benefit certain conventional percutaneous transluminal coronary angioplasty (PTCA) procedures. In accordance with the method of the present invention, the variable diameter balloon **18** is percutaneously advanced and positioned such that the central segment **30** of the balloon **18** is adjacent a vascular treatment site. Generally, the treatment site is a stenosis such as due to a plaque or thrombus. The variable diameter balloon **18** is inflated to a first inflation profile to begin dilation of the stenosis. Preferably, the first inflation profile is achieved by applying up to about 6 ATM of pressure to the balloon **18**. At the first inflation profile, the entire balloon is inflated to the inner diameter of the vessel, thus restoring patency to the vascular lumen. In one embodiment, the variable diameter balloon **18** is inflated to a first inflation diameter, of about 2.5 mm, at an inflation pressure of 6 ATM. The first inflation diameter is preferably about the native diameter of the vessel.

As additional pressure is applied to the variable diameter balloon **18**, a second inflation profile is achieved wherein the central segment **30** of the balloon **18** expands beyond the diameter of the first inflation profile to a second inflation diameter, while the proximal segment **26** and the distal segment **28** remain at or substantially at the first inflation diameter. As the pressure applied to the variable diameter balloon **18** increases, the diameter of the central segment **30** of the balloon **18** extends past the native diameter of the vessel to the second inflation diameter. Utilizing this method, and depending upon the balloon size selected, the stenosis is compressed to a point which is beyond the native diameter of the vessel. In a preferred embodiment, at an applied pressure of 11 ATM the diameter of the central segment **30** of the balloon **18** at the second inflation diameter is 3 mm and the diameter of the proximal end **26** and the distal end **28** at the first inflation diameter is approximately 2.5 mm. Second inflation diameters in between the first inflation diameter and the maximum inflation diameter can be readily achieved by controlling inflation pressure, as illustrated for one embodiment in Table 2, above.

After the stenosis is compressed to or beyond the native diameter of the vessel, the balloon is evacuated and the catheter withdrawn. Alternatively, if desired, the pressure is reduced until the balloon **18** resumes the first inflation profile. At this point, the balloon **18** may be held at the first inflation diameter for short periods to continue to maintain patency of the lumen if short term rebound is a concern. This post dilatation step is preferably accomplished using a catheter having perfusion capabilities. Finally, the remaining pressure applied to the balloon **18** is reduced causing the variable diameter balloon **18** to deflate. The catheter is then extracted from the vessel utilizing conventional PTCA procedures.

The "focal" or "differential compliance" balloon of the present invention provides important real time diagnostic information about the lesion being treated. In a balloon having one or more noncompliant or substantially noncompliant zones such as proximal segment **26** and distal segment **28** and a central focal segment **30**, (FIG. 2) inflation within a lesion will proceed through a series of discreet phases. The phases can be visually differentiated by observing the balloon fluoroscopically and comparing the apparent diameter of the central section with the diameter of the one or more substantially noncompliant zones. The substantially noncompliant zones may be considered reference zones for present purposes.

When the balloon **18** is inflated within a lesion, the reference zone will normally be positioned proximally or distally of the lesion and the central zone will be centered within the lesion. As balloon inflation begins, the overall balloon may take on a "dog bone" shape with the central portion radially inwardly restrained by the lesion. As inflation pressure is increased, the central section will tend to expand until the balloon has assumed an overall generally cylindrical profile. At a certain higher pressure, the balloon will focalize, such that the central region has reached its second, larger inflated diameter. By observing the first pressure at which the balloon assumes a generally cylindrical configuration and the second higher pressure at which the balloon focalizes, the clinician can learn important information about the morphology of the lesion.

For example, in a balloon rated 3.0 mm at 6 atmospheres, the reference zone may grow to 3.2 mm at 11 atmospheres. The focal section will grow to 3.0 mm at 6 atmospheres, and, in a healthy artery, should grow to 3.5 mm at 11 atmospheres. If there has been no focalization at 11 atmospheres, the clinician will know that the lesion is highly calcified or is otherwise highly resistant to expansion. The pressure can then be gradually increased up to a maximum pressure which approaches the burst pressure, and the pressure at which focalization is finally visualized will reveal information about the degree of calcification or other information about the lesion.

Thus, there is provided in accordance with the present invention a method of obtaining characterizing information about a lesion. The characterizing information is obtained by positioning a differential compliance balloon in the artery such that a central focal section is positioned within the lesion. The balloon is inflated to a first inflation pressure such that the balloon achieves a "dogbone" configuration with the lesion. The clinician preferably notes that first pressure. The pressure is increased until the balloon achieves a generally cylindrical exterior configuration. The pressure at which the substantially cylindrical configuration is achieved is preferably noted. The pressure in the balloon is increased further until focalization of the central section is achieved, and the focalization pressure is noted. One or more of the noted pressures may be compared to other information concerning the same patient or against reference data to assess the nature of the lesion. Since the balloon can be readily fluoroscopically visualized, the clinician receives real time information about the size of the inflation balloon merely by visually comparing the focal section with the reference section. If, at a particular pressure, the balloon is "straight across" (i.e. has not focalized) the clinician can look at the reference chart for the balloon or rely upon experience to assess the diameter of the vessel at the treatment site.

In accordance with another aspect of the present invention, there is provided a method of interactive angio-

plasty using the differential compliance balloon of the present invention. In general, the interactive angioplasty method involves inflating the balloon to a first inflation pressure, which should produce a first inflation profile for a particular expected lesion morphology. If the profile of the balloon at the first inflation pressure is different than the expected first inflation profile, the clinician will know that the lesion morphology may be different than anticipated. The clinician can thus responsively change the course of treatment, such as by removing the catheter and replacing it with a different one.

For example, if a highly calcified or fibrotic lesion is expected and the first inflation pressure produces a substantially cylindrical balloon rather than a dogbone shaped balloon, the clinician may determine that the balloon selected was too small or the lesion was not calcified or fibrotic as expected. That balloon catheter may be withdrawn and a catheter having a larger balloon thereafter positioned in the lesion. If the expected degree of inflation at the focal zone (compared, for example, to the reference zone) fails to occur at the expected inflation pressure, the clinician may alternatively elect to increase the inflation pressure, thereby exerting a greater force on the lesion.

Alternatively, lesion morphology information obtained by comparing the expected inflation profile at a given pressure stage with the actual inflation profile may cause the clinician to seek alternate treatment, such as drug therapy, surgery, or other techniques that may be available at the time. More rapid progression than expected from dogbone to cylindrical to focalized inflation may indicate the presence of soft placque or of a thrombosis, and measures can be taken in response to minimize the risk of over dilatation or embolization. These measures may include drug therapy such as local administration of streptokinase or TPA, or other measures such as atherectomy, laser therapy or stenting.

One of the advantages of the interactive angioplasty of the present invention is that the clinician can alter the course of treatment during the procedure, in response to information obtained during the procedure about lesion morphology or progression of the procedure. For example, if the balloon fails to focalize at the pressure previously expected to produce focalization, depending upon other circumstances of the patient, the clinician may determine that further dilatation of the lesion will produce an undesirable dissection of the artery, and a different treatment may be indicated. Alternatively, the clinician may elect to simply increase the inflation pressure until focalization occurs, or substitute a different balloon having a different inflation diameter or capable of sustaining a greater inflation pressure.

At each of the reference points identified previously herein, such as the dogbone profile, the cylindrical profile, and the focalized profile, any deviation from the expected pressure to achieve that profile can thus be noted by the clinician and used to assess the course of further treatment. The interactive angioplasty method of the present invention can be accomplished both in the context of balloon dilatation and also in the context of implantation and or sizing of an intervascular prosthesis (stent).

Pressure response data for a series of exemplary balloons manufactured in accordance with the present invention using techniques described previously herein is provided in Table III below. The compliance curves for a reference zone and a focal zone of a differential compliance balloon rated for 3.5 mm at 6 atmospheres are illustrated in FIG. 5.

TABLE III

EFFECT OF INCREASED PRESSURE ON BALLOON DIAMETER			
Balloon	11 ATM	14 ATM	16 ATM
3.0 mm			
Reference Zone	3.2 mm	3.2 mm	3.3 mm
Focal Zone	3.5 mm	3.5 mm	3.5–3.7 mm
3.5 mm			
Reference Zone	3.7 mm	3.7 mm	3.8 mm
Focal Zone	4.0 mm	4.0 mm	4.0–4.2 mm
4.0 mm			
Reference Zone	4.2 mm	4.2 mm	4.3 mm
Focal Zone	4.5 mm	4.5 mm	4.5–4.7 mm

As exemplified in Table III, the reference zones on a particular balloon are expected to have a predetermined diameter at certain pressures. For example, the reference zones on a 3.0 mm balloon are expected to inflate to 3.2 mm at 11 ATM. If the balloon appears to be "straight across" at 11 ATM, the clinician knows that the focal section and therefore the lesion has been inflated to 3.2 mm. If the balloon has focalized, the clinician knows that the lesion has been inflated to 3.5 mm by referring to a look up table containing the balloon specifications. If focalization does not occur until a higher pressure such as 14 ATM has been reached, the clinician still knows that the lesion has been inflated to 3.5 mm, but also knows that the lesion was relatively calcified or fibrotic.

The present interactive angioplasty invention thus enables the clinician to take into account the difference in balloon inflation characteristics between the in vitro and in vivo environments. Balloons in vitro exhibit a predictable inflation response to pressure. Balloon inflation in vivo, however, can be quite different from the balloon rating, and also from lesion to lesion, as a result of the differences in vessel wall thickness, lesion morphology and other characteristics that affect the resistance to radial expansion in the area of the target lesion. By providing reference information such as the inflated diameter of the reference and focal zones of a balloon at each of a series of pressures, the clinician can determine the actual diameter of the balloon in the focal zone by observing the balloon in either of the "straight across" or focalized inflation profiles.

The differential compliance balloon of the present invention is also particularly suited for the implantation and or sizing of intravascular stents. For example, in a 3.2 mm vessel, it may be desirable to dilate a stent to 3.5 mm inside diameter since some stents tend to recoil in vivo. If the balloon is inflated up to 10 ATM with no focalization, the clinician knows to increase the pressure until a focal section becomes apparent. When the focal section has become apparent, the clinician will know that the inside diameter of the stent has been appropriately inflated to 3.5 mm.

In accordance with a further aspect of the present invention, there is provided a method of implanting a tubular stent within a body lumen. Tubular stents of the type adapted to be carried to a vascular site on a balloon catheter, and for expansion from a first insertion diameter to a second implanted diameter are well-known in the art.

In accordance with the method of implanting a tubular stent, an expandable stent is positioned about the deflated balloon of a variable diameter balloon catheter in accordance with the present invention. The balloon is thereafter

percutaneously inserted into the vascular system and transluminally advanced to position the stent at the treatment site. The balloon is thereafter inflated to at least a first inflation configuration, wherein the balloon exhibits a substantially cylindrical profile throughout its axial length. Thereafter, the balloon is optionally inflated to a second inflation profile, thereby inflating at least a portion of the stent to a second, greater diameter. Depending upon the etiology of the underlying condition, the central region of the stent may preferentially be inflated to a larger diameter than either of the axial ends of the stent. Alternatively, the axial length of the stent is selected to approximately equal the axial length of the focal zone on the inflation balloon. In this manner, the inflation balloon within the stent is expandable to a diameter slightly larger than the native diameter of the adjacent vessel. This permits subsequent overgrowth of endothelium along the interior wall of the stent while still leaving a lumen having an interior diameter within the stent approximately equal to the native diameter of the lumen adjacent the stent.

In accordance with a further aspect of the present invention, the variable diameter balloon is utilized to "tack down" a previously positioned tubular stent. In accordance with this aspect of the present invention, a tubular stent is identified within a body lumen. The focal balloon is positioned within the stent in accordance with conventional PTCA procedures, and the balloon is inflated so that the central, focal section enlarges the diameter of at least a first portion of the stent. The balloon is thereafter reduced in diameter, and, preferably, repositioned within a second region within the stent and then reinflated to expand at least the second region of the stent. Expansions of this type can be repeated until the stent has been expanded as desired. The balloon is thereafter evacuated and removed from the patient.

In accordance with a further aspect of the present invention, there is provided a method of percutaneous transluminal angioplasty in which multiple lesions of differing sizes are dilated without removing the catheter from the body. In accordance with this aspect of the present invention, the variable diameter balloon is positioned within a first stenosis in accordance with conventional PTCA techniques. The balloon is dilated to a sufficient diameter to restore patency to the vascular lumen. The balloon is thereafter deflated, and repositioned within a second stenosis in the vascular system. The balloon is inflated to restore patency of the vessel in the region of the second stenosis. Optionally, the balloon may be deflated, and repositioned within a third stenosis in the body lumen. The balloon is then inflated to a sufficient diameter to restore patency in the body lumen in the region of the third stenosis. Four or more lesions can be treated seriatim in this manner.

Preferably, the balloon is inflated to a first diameter in the first stenosis, and to a second, different diameter, in the second stenosis. In this manner, multiple dilatations at different diameters can be accomplished utilizing the balloon of the present invention. This method is accomplished by supplying a first inflation pressure to the balloon while the balloon is positioned in a first position in the vascular system, and thereafter supplying a second pressure to the balloon when the balloon is in a second position in the vascular system. In accordance with the previous disclosure herein, each of the first and second inflation pressures is selected to achieve a preselected inflation diameter of the balloon.

A number of the advantages of the interactive angioplasty methods and stent implantation and sizing methods of the present invention can also be accrued through the use of an alternate embodiment of the balloon of the present invention as illustrated in FIG. 7. Referring to FIG. 7, there is disclosed a fixed focal balloon 64. By "fixed" focal balloon, it is meant that the balloon assumes a stepped configuration in its initial in vitro inflated profile. Increased inflation pressure beyond the pressure necessary to achieve the initial stepped inflation profile does not appreciably change the relative proportionality of the profile from its initial stepped configuration.

The stepped configuration is characterized by a difference in diameter between at least one reference zone and a focal zone, preferably on the same balloon. The fixed focal balloon of the present invention can be constructed using either relatively compliant or relatively noncompliant materials, with the resulting characteristics that will be readily apparent to those of skill in the art in view of the disclosure herein. Preferably, the fixed focal balloon comprises polyethylene terephthalate.

The embodiment of the fixed focal balloon 64 illustrated in FIG. 7 has a central focal zone and a proximal as well as a distal reference zone. However, the present inventors also contemplate fixed focal balloons in which either the proximal reference zone or the distal reference zone is omitted. These embodiments include only a single reference zone and a single focal zone. The reference zone may be positioned either proximally or distally of the focal zone.

For example, in one two segment embodiment of the present invention, a proximal segment on the balloon is inflatable to a greater diameter than a distal segment. In general, the proximal segment will inflate to a generally cylindrical configuration in an unconstrained inflation. A transition zone is disposed at the distal end of the proximal segment. In the transition zone, the diameter of the balloon steps down to the smaller inflated diameter of the distal segment. The axial lengths and diameters of the proximal and distal segments can vary widely depending upon the intended use of the balloon. In one application, the balloon is used to size or implant two stents positioned end to end in a vessel. The stents may comprise a pair of 15 mm length stents or 20 mm length stents or otherwise as may be desired. For this application, the balloon may have an overall length of from about 20 mm or 30 mm to about 40 mm or greater. In one 30 mm balloon, a proximal segment is approximately 15 mm long and has an inflated diameter of about 3.5 mm. At the distal end of the proximal segment is a transition zone which will be generally be less than 1 or 2 mm in length and preferably about a ½ mm in length. Distally of the transition zone is a second segment approximately 15 mm in length and having an inflated diameter of about 3.0 mm. Alternate pairs of proximal and distal segment inflated diameters may also be utilized as will be appreciated by those of skill in the art. In general, the difference in diameter between the proximal and distal segments will be within the range of from about 0.2 mm to about 1 mm, and, preferably, will be about 0.5 mm. Proximal and distal segment diameter and pairs for balloons believed useful by the present inventor include 4.0/3.5 mm, 3.5/3.0 mm, 3.0/2.5 mm. Proximal and distal balloon zone lengths are preferably approximately equal in a given balloon, e.g., 20 mm/20 mm in a 40 mm balloon, although dissimilar zone lengths may be desirable in particular specialty applications.

As a further alternative, the balloon is provided with three stepped diameters in the inflated profile. In a 30 mm balloon, for example, a proximal 10 mm section inflates to a first diameter, an intermediate 10 mm section inflates to a second diameter and a third 10 mm section inflates to a third diameter. Preferably, the first, second and third diameters

decrease in the distal direction. The diameters of adjacent sections may be separated by 0.5 mm, 0.25 mm, or other differential as may desired for the intended application. Thus, in an exemplary balloon, the first diameter is 3.5 mm, the second diameter is 3.0 mm and the third diameter is 2.5 mm. In an alternate example, the first diameter is 3.5 mm, the second diameter is 3.25 mm and the third diameter is 3.0 mm. Similar gradations from about 2 mm up through about 4.5 mm for coronary applications, and up to 8 or more millimeters for other applications may be used.

Any of the preceding multizone balloons, particularly the two zone and three zone balloons can be utilized to implant or size a single "long" stent or expandable graft. For present purposes, long stents will have an axial length of greater than about 20 mm, and could have any of a variety of lengths such as 25, 30, 35, 40, 45, 50, 55, 60 mm or longer. Corresponding balloon lengths are also contemplated. Stent and balloon lengths intermediate the foregoing dimensions may also be utilized, as will be appreciated by those of skill in the art. Two or three or four or more axially adjacent stents may also be implanted or sized using the catheters described herein.

Any of the balloon catheter designs described herein may be utilized in the method of implanting a tubular stent, the method of sizing a previously implanted stent, or simultaneously implanting and sizing tubular stents (which term is intended to include grafts throughout). The balloon catheters disclosed herein are also useful in the methods of simultaneously implanting and/or sizing multiple stents.

Alternatively, the proximal and distal zones in a three zone balloon may be inflatable to the relatively larger diameter, while the central zone is inflated to the smaller, reference diameter. This embodiment may be considered to have a proximal and a distal focal zone and a single central reference zone. These and additional variations are illustrated in FIGS. 8–18, discussed infra. The desirability of one combination over another will be governed by the requirements for a particular balloon dilatation or stent or graft implantation procedure as will be apparent to those of skill in the art in view of the disclosure herein.

Referring to the embodiment illustrated in FIG. 7, the fixed focal balloon 64 is provided with a proximal reference zone 66, a central focal zone 68 and a distal reference zone 70. The relative lengths of each of these zones may vary considerably depending upon the intended use of the balloon. In general, any of the dimensions of the balloon, both in terms of diameters and lengths as well as other catheter dimensions, may be the same as those disclosed in connection with other embodiments previously disclosed herein. In one particular application, the focal zone 68 has an axial length of 10 millimeters, and each of the proximal zone 66 and distal zone 70 has an axial length of about 5 millimeters. At 8 atmospheres inflation pressure, the proximal reference zone 66 has an outside diameter of about 3 millimeters, and the focal zone 68 has an outside diameter of about 3.4 millimeters. The same balloon at 18 atmospheres inflation pressure has an outside diameter of about 3.1 millimeters in the proximal reference zone 66 and an outside diameter of about 3.5 millimeters in the focal zone 68. That particular balloon was constructed from PET, having a wall thickness of about 0.0006–0.0008 inches.

Depending upon the desired clinical performance of the balloon, the relative expansion characteristics of the reference zone compared to the focal zone can be varied. For example, although the focal section will normally retain a larger inflated diameter than the reference zone, the refer-

ence zone may grow in response to an increase in inflation pressure a greater amount than the focal zone. In one PET balloon, having a wall thickness in the range of from about 0.0006 to about 0.0008 inches, the growth of the reference zone upon an increase in inflation pressure from 8 to 18 atmospheres was about 0.2610 millimeters. The growth in the focal zone over the same pressure increase was about 0.1457 millimeters. It may alternatively be desired to achieve a greater growth in the focal zone compared to the reference zone, or an equal growth in each zone as a function of increased pressure. Optimizing the growth response to increased pressure of the focal zone relative to the reference zone for any particular intended application can be accomplished by the exercise of routine skill in the art in view of the disclosure therein.

The fixed focal balloon 64 further comprises a first transition 72 which steps the diameter of the balloon up from the diameter of the catheter shaft 74 to the diameter of the proximal reference zone 66. All balloons have some form of transition, such as first transition 72, and the reference zone 66 is to be distinguished from what is simply a transition, such as transition 72. Thus, the reference zone 66 is provided with a visibly discernable generally cylindrical exterior configuration in the inflated state, or other characteristic inflated configuration, so that it can be distinguished visibly from the transition 72 in vivo. Thus, the proximal reference zone 66 can be either a cylindrical section which transitions sharply into a generally conical transition section, such as first transition 72. Alternatively, the reference zone 66 may comprise a continuation of a first transition 72, but with a visibly different angle with respect to the longitudinal axis of the catheter when compared to the angle of the surface of the first transition 72 taken in the axial direction. In one embodiment of the invention, the surface of the first transition 72 measured in the axial direction lies at an angle of approximately 20 degrees with respect to the longitudinal axis of the catheter shaft 74.

A second transition 76 is provided to step the diameter of the inflated balloon from that of the proximal reference zone 66 to the focal zone 68. A third transition 78 is provided to step the outside diameter of the inflated balloon from the diameter of focal zone 68 down to the diameter of distal reference zone 70. The angle of each of the second and third transition sections can vary depending upon desired performance and design characteristics, but in one embodiment of the invention have a surface which lies on a plane extending in the axial direction at an angle of about 11° from the longitudinal axis of the catheter shaft 74. The axial length of each of the second transition 76 and third transition 78 will vary depending upon the difference in diameter of the focal zone from the reference zone, but will generally be within the range of from about 0.5 mm to about 4 mm.

A fourth transition 80 is provided to step the diameter of the balloon 64 from that of the distal reference zone 70 back down to the diameter of the distal catheter shaft or tip 82.

The three zone embodiment illustrated in FIG. 7 can be produced having any of a variety of dimensions, depending upon the particular contemplated end use of the catheter. In the following nonlimiting examples of balloon dimensions, the dimensions for the balloon are recited at 8 atmospheres inflation pressure in an unrestrained (in vitro) expansion.

For example, balloons can be readily provided having a focal zone 68 inflatable to an initial inflation diameter of anywhere within the range from about 1.5 mm to about 10 mm. For coronary vascular applications, the focal zone will normally be inflatable to a diameter within the range from

about 1.5 mm to about 4 mm, with balloons available at every 0.25 mm increment in between.

The reference zone, such as proximal reference zone **66** and/or distal reference zone **70** is preferably inflatable to a diameter within the range from about 1.25 mm to about 9.5 mm. For coronary vascular applications, the reference zone is preferably inflatable to a diameter within the range of from about 1.25 mm to about 3.5 mm.

The focal zone is normally inflatable to a generally cylindrical profile, which has a diameter that is greater than the diameter in the reference zone. Neither the focal zone nor the reference zone or zones need to be precisely cylindrical. Thus, the present invention can still be accomplished with some slight curvature or bowing of the surface of the focal zone or reference zone taken along the axial direction.

In general, the maximum diameter of the focal zone will be within the range of from about 7% to about 30% percent or more greater than the average diameter of the reference zone. Preferably, the maximum diameter in the focal zone will be at least about 10% greater than the average diameter in the reference zone.

The configuration of the reference zone compared to the focal zone can be varied considerably, as long as the reference zone and the focal zone outer diameters can be visualized by the clinician using conventional fluoroscopic or other visualization techniques. Thus, although the reference zone can take on a slightly conical configuration such that it ramps radially outwardly in the direction of the focal zone, it should not be to such an extent that the clinician cannot visually differentiate the inflation profile of the focal zone compared to the reference zone in vivo.

The function of the reference zone, to provide a visual reference to indicate the relative inflation of the focal zone, can be accomplished by the provision of radio opaque markers at either end of or within the balloon. For example, inflatable or flexible radio opaque markers may be provided along the transition in a balloon from the catheter shaft to the working zone in an appropriate position along the ramp such that, when the balloon is inflated, the radio opaque marker provides a visual indication of a predetermined diameter. Alternatively, the use of radiopaque inflation media to inflate the balloon can also permit in vivo visualization.

Although the preferred embodiments described above rely upon the balloon to provide a visual reference, the objectives of the present invention may be accomplished using other visual indica which will permit the clinician to assess the relative in vivo inflation of the focal zone. Thus, in a broad sense, the invention contemplates a visualizable aspect associated with the focal section and a visualizable reference indica such as the balloon, a radiopaque marker on or associated with the balloon, radiopaque inflation media, or others, which allows the clinician to compare the diameter of the focal section relative to some other visual reference.

In addition to the provision of a visual reference to allow the clinician to assess the inflated diameter of the balloon, the balloon of the present invention provides a way to focalize the balloon inflation energy at a predetermined position along the balloon. The axial length of the focal section can be varied considerably, depending upon the desired axial length along which inflation energy is to be focalized. For example, the axial length of the focal section may be anywhere within the range of from about 0.5 cm to about 5.0 cm. For coronary vascular applications, the axial length of the focal balloon will normally be within the range of from about 0.5 cm to about 2.0 cm for performing conventional PTCA. The axial length will normally be

within the range of from about 0.5 cm to about 5 cm for implanting expandable tubular stents, depending upon the length of the desired stent. Normally, the axial length of the focal section will be greater than the axial length of the stent.

A variety of focal balloon catheters of the present invention are preferably available to the clinician having an array of different axial focal lengths, so that a balloon having the appropriate focal length can be selected at the time of the procedure based upon the nature of the procedure to be performed, and the location in the vasculature. For example, in a curved portion of the artery, the clinician may wish to minimize the axial length of the focal zone to the extent possible while still having a sufficient axial length to accomplish the dilatation or stent implantation procedure. An excessive axial length in the inflated balloon for a given curved vessel can elevate the risk of vascular dissection as is well known in the art.

The axial length of the reference zone can also be varied considerably, depending upon the desired performance characteristics. In general, it has been found that axial lengths of at least about 3 mm allow ready visualization by the clinician. Axial lengths much shorter than 3.0 mm may require too much effort to observe under fluoroscopic conditions, and the reference function of the reference zone may thus not be readily accomplished.

In one embodiment of the invention, produced in accordance with the three-zone illustration of FIG. **7**, the proximal and distal reference zones each have an axial length of about 5.0 mm and an inflated diameter of about 3.0 mm at 8 ATM. The axial length of the focal zone, including the length of the second transition **76** and third transition **78**, is about 8 mm. The diameter of the focal zone at 8 atmospheres inflation pressure is about 3.5 mm.

The fixed focal balloon **64** can be manufactured using any of a variety of techniques which will be understood to those of skill in the art. For example, the balloon can be manufactured by blowing suitable tubing stock into a stepped mold cavity. Alternatively, the tubing stock can be blown into a first mold having a diameter approximately equivalent to the reference diameter. The balloon can then be blown into a second mold having a larger diameter section corresponding to the focal section in the finished balloon. The balloon is inflated into the larger mold under the application of heat, as will be understood by those of skill in the art.

The fixed focal balloon **64** of the present invention or other fixed focal balloons as described herein can be utilized in any of the methods described in connection with the differential compliance balloons of the present invention. Thus, the real-time diagnostic information about the lesion which is obtainable through the use of the focal or differential compliance balloons described in connection with FIGS. **1–6** herein can also generally be achieved using the embodiment of FIG. **7**. Unless clearly specified to the contrary, the various methods of the present invention, including both the differential compliance and stent implantation and sizing methods, are intended to be accomplished by either the fixed focal balloon or the variable focal balloon embodiments of the methods of the present invention.

FIGS. **8–18** illustrate a variety of specialized focal and/or compliant zone balloons in accordance with the present invention. These balloons can incorporate any of the structures, features, and methods of the previous embodiments as may be desirable for particular intended applications. Therefore, construction techniques, materials, dimensions, capabilities and methodology discussed above applies to the following embodiments, but will generally not be repeated below.

5,843,116

21

An alternate multi-zone balloon design of the present invention is schematically illustrated in FIGS. 8 and 9. Referring to FIG. 8, there is disclosed a catheter having an elongate flexible tubular shaft 84 such as has been discussed in connection with previous embodiments. The catheter shaft 84 is provided with a guidewire lumen 85 and at least one inflation lumen 86. Guidewire lumen 85 terminates in a distal opening 87 at the distal end 88 of the catheter.

A distal region on the catheter is provided with a balloon assembly 89. The balloon assembly 89 comprises an inner inflatable balloon 90 disposed within an outer inflatable balloon 91. Inflation lumen 86 provides fluid communication between a proximal source of inflation media (not shown) and the interior of the inner balloon 90. The construction materials, construction techniques and dimensions of the various components of the various balloons and catheters illustrated in FIGS. 8 through 18 can be the same or similar to as those disclosed in connection with previous embodiments. For example, the inner balloon 90 may be constructed from a relatively noncompliant material such as PET or a relatively compliant material such as polyethylene.

The balloon assembly 89 is configured to produce a three zone balloon of the type that has been previously discussed, such that the balloon assembly 89 is inflatable first to a generally cylindrical configuration as illustrated in FIG. 8 and, thereafter, to a stepped configuration such as that illustrated in FIG. 9. Thus, a focal zone 92 (also referred to herein as a compliant zone) is disposed adjacent one or more reference zones, such as proximal reference zone 93 and distal reference zone 94.

In this embodiment, the inner balloon 90 and outer balloon 91 are designed to substantially maintain contact with each other, except in the region of the focal section 92 once that section has focalized. Inner balloon 90 and outer balloon 91 may be maintained in contact at their proximal and distal ends such as by the use of thermal bonding, adhesives, or other techniques described elsewhere herein. In addition, expansion limiting bands as have been previously discussed may also be incorporated into the balloons illustrated in FIGS. 8 and 9, such as in the reference zones 93 and 94.

One feature which distinguishes the balloon illustrated in FIGS. 8 and 9 from those previously discussed is the provision of one or more apertures 95 for providing communication between the interior 96 of balloon 90 and the interior 97 of outer balloon 91. Apertures 95 permit a rate controlled diffusion of inflation media from the interior 96 of balloon 90 into the space 97 to provide a delayed, gradual focalization of the focal section 92. In use, the foregoing features permit the clinician to inflate the balloon assembly 89 to a preselected pressure, which will cause the balloon assembly 89 to inflate to its generally cylindrical inflation profile. Migration of inflation media through the ports 95 then cause the compliant section 92 to gradually inflate to the second, stepped configuration of the balloon assembly as illustrated in FIG. 9.

Preferably, a plurality of discrete ports 95 is provided in the balloon 90 to enable the diffusion of inflation media at a desired rate into the focal section 92. The ports 95 are preferably each within the range of from about 50 microns to about 400 microns across, and more preferably are within the range of from about 100 to about 300. In one embodiment, the ports are about 250 microns in diameter. Depending upon the desired rate of focalization, there are preferably anywhere from about 5 to about 50 inflation ports 95 on the inner balloon 90. Alternatively, a different number

22

of ports and/or port diameters can be used depending upon the desired inflation characteristics of the balloon as a function of time. The number and size of the inflation ports 95 thus can be optimized for a particular desired inflation characteristic, taking into account the viscosity of the inflation media at the temperature the media is likely to be during an anticipated procedure.

In one embodiment, the outer balloon 91 comprises a relatively noncompliant material, which is preformed into the second, stepped configuration. In this embodiment, a relatively high pressure can be introduced into inner balloon 90. Inflation media will diffuse through ports 95 into the focal zone 92, thereby causing the balloon to assume its second, stepped configuration substantially without actual expansion of the material of the focal section 92. Alternatively, at least the focal zone 92 of the outer balloon 91 and preferably the entire balloon 91 comprises a relatively compliant material as has been discussed, so that the focal zone 92 grows by stretching in response to pressure as inflation media diffuses across inflation ports 95.

Referring to FIG. 10, there is illustrated a schematic outer profile of a distally tapered balloon 100 which may be utilized in connection with any of the embodiments disclosed elsewhere herein. In general, the outer profile comprises a focal zone 98, which may or may not be compliant. The focal zone 98 is adjacent at least one reference zone 99. In this embodiment, the reference zone 99 is disposed proximally of the focal zone 98. A distal section 101 is provided on the balloon distally of the focal section 98. Distal section 101 in the illustrated embodiment comprises an elongate tapered section which reduces in cross-sectional area in the distal direction. As an alternate embodiment, distal section 101 may comprise a generally cylindrical configuration, having a cross-sectional area in its inflated configuration which is smaller than the cross-sectional area of the proximal reference zone 99.

The above described modification to the exterior profile illustrated in FIG. 10 would thus produce a balloon having a configuration similar to that illustrated in FIG. 3. However, the distal cylindrical section or reference zone has a diameter which is less than the proximal cylindrical reference zone. In general, the inflated diameter of the distal reference zone will be no more than about 95% of the diameter of the proximal reference zone. Preferably, the inflated diameter of the distal reference zone will be no more than about 80% of the inflated diameter of the proximal reference zone. In one embodiment, the inflated diameter of the distal reference zone is about 3.0, the inflated focalized diameter of the focal section is about 3.5 and the inflated diameter of the proximal reference zone is about 3.25, at about 12 atmospheres.

Both of the foregoing modified distal segment configurations take into account the anatomical environment encountered during certain dilatations. For example, the native lumen in an artery on the catheter's distal side of the lesion is often smaller in diameter than the native lumen on the catheter's proximal side of the lesion. Provision of a distal section 101 having a step reduction or a tapered reduction in the inflated diameter can permit the catheter to accomplish all of the desired functions, while at the same time reducing the risk of dissection of the artery. In addition, the tapered distal section such as the embodiment illustrated in FIG. 8 may facilitate treatment of lesions or implantation of stents in or adjacent a curved segment of the artery, as will be apparent to those of skill in the art in view of the disclosure herein.

Referring to FIG. 11, there is disclosed a schematic illustration of a two inflation lumen catheter for use with

certain embodiments of the balloons of the present invention. The catheter **102** comprises an inflatable balloon assembly **103** at its distal end as has been discussed. The catheter **102** is further provided with a manifold **104** having a guidewire access port **105** in an over the wire embodiment. As has been discussed, rapid exchange embodiments may also be constructed in which the proximal guidewire access port **105** is located along the length of the catheter shaft **102**, such as in the area of about 20 or 25 centimeters proximally of the distal end of the catheter. In either embodiment, the distal end of the guidewire lumen typically exits the catheter at a distal port **106**.

The manifold **104** in this embodiment is provided with a first inflation port **107** and a second inflation port **108** for communicating with a first inflation lumen **109** and a second inflation lumen **110**, respectively.

Referring to FIG. **12**, the first inflation lumen **109** is in fluid communication with the interior **112** of an inner balloon **114**. The second inflation lumen **110** is in fluid communication with the potential space between the inner balloon **114** and an outer balloon **116**. As has been previously discussed, inflation of the inner balloon **114** will in most embodiments cause the inner balloon **114** to assume a generally cylindrical inflated configuration. Inflation thereafter of the second balloon **116** will cause the second balloon **116** to assume a focalized configuration such as that illustrated in FIG. **13**.

In an embodiment in which the outer balloon **116** is made from a relatively noncompliant material and preformed to have its stepped configuration, the outer balloon **116** need not necessarily be secured to the inner balloon **114**. Thus, a small space may exist in the inflated configuration as illustrated in FIG. **13** between the outer balloon **116** and the inner balloon **114** in the proximal and distal segments. Alternatively, as has been discussed, the inner and outer balloons may be secured together in the proximal and distal zones, depending upon the desired balloon construction materials and performance characteristics.

In an embodiment where the inner balloon **114** and outer balloon **116** are secured together, a flow passage way **118** from the inflation lumen **110** to the focal section **120** can be readily provided such as by insertion of a mandril through the inflation lumen **110** and in between the balloons **114** and **116** prior to the method step of securing the balloon together. Proximal withdrawal of the mandril (not illustrated) will thereafter produce a flow passage way **118** as will be appreciated by those of skill in the art.

A variation of the embodiment of FIG. **13** is illustrated in FIG. **14**. In this embodiment, a plurality of delivery ports **122** are illustrated in the focal section **120** of the outer balloon **116**. Delivery ports **122** will facilitate the site specific delivery of substances to the vessel wall, such as drugs, or other diagnostic or therapeutic media as may be desired. This embodiment of the present invention may be constructed and utilized in a variety of manners similar to those disclosed in U.S. Pat. No. 5,421,826 to Crocker, et al., the disclosure of which is incorporated herein by reference.

As has been referenced, supra, a multizone balloon including the technology of the present invention may desirably include a proximal and a distal focal or compliant section, and a central reduced diameter section. Two embodiments of the present invention incorporating this feature are illustrated in FIGS. **15** and **16**.

Referring to FIG. **15**, there is disclosed a dual-lobed balloon catheter **130**, comprising a single balloon **138** having a proximal lobe **140** and a distal lobe **142**. By "single balloon" it is meant that the two or more lobes of the balloon may be inflated by way of a single inflation lumen. The actual balloon may comprise a single layer or a plurality of layers, depending upon the desired construction technique. For example, either one or each of the proximal lobe **140** and distal lobe **142** may have two or more layers, expansion limiting bands, or other structures as disclosed elsewhere herein. A central zone of reduced inflated diameter **144** is disposed between the proximal zone **140** and distal zone **142**.

The balloon **138** is preferably mounted on an elongate flexible catheter shaft **132**. Catheter shaft **132** is preferably provided with a guidewire lumen **134** and at least one additional lumen **136** such as for inflation of the balloon **138**. Each of the proximal and distal lobes **140** and **142** may have any of the dimensions discussed in accordance with previous embodiments. In addition, either or both of the proximal and distal lobes **140** and **142** may comprise a compliant construction or a substantially noncompliant construction as has been discussed.

For example, balloon construction techniques disclosed previously herein can be utilized to produce a dual-lobed balloon **138** in which the proximal lobe **140** and distal lobe **140** inflate to a diameter of, e.g., about 2.5 millimeters at six atmospheres. As inflation pressure is increased to, for example, 14 atmospheres, either or both of the proximal and distal lobes may be restrained from expanding beyond about 2.6 or 2.7 millimeters. Alternatively, the proximal or the distal lobe **140** or **142** or both may expand to as much as about 3.3 millimeters or more at 14 atmospheres.

Selection of which of the proximal lobe **140** and distal lobe **142** to be expandable to a greater inflated diameter will depend upon the intended use of the catheter. For example, in most coronary vascular applications, the artery descends in diameter in the catheter distal direction. Thus, it may be desirable for the proximal lobe **140** to be inflatable to a larger final diameter. Alternatively, applications of the balloon catheter **130** for such things as drug or other media infusion, heart valve replacement or repair, or other uses will require different dimensional relationships between the proximal lobe **140** and distal lobe **142** as will be apparent to those of skill in the art in view of the disclosure herein.

The central zone **144** can have an inflated diameter anywhere within the range of from about the outside diameter of the catheter shaft to about 2.8 mm in a catheter for coronary vascular applications having a proximal balloon **140** with an inflated diameter of about three millimeters. The diameter of central section **144** may be constrained such as through the use of expansion limiting bands as has been discussed, or through the use of cross-linking techniques also discussed above. Alternatively, the central section **144** may be adhered to the catheter shaft **132**, leaving only one or more axially extending flow paths for placing the interior of lobe **140** in fluid communication with the interior of lobe **142**.

Referring to FIG. **16**, the dual balloon counterpart to the design illustrated in FIG. **15** is disclosed. In general, dual balloon catheter **148** comprises a proximal balloon **150**, a distal balloon **152** and a central zone **154** separating the proximal and distal balloons. The balloons are mounted on an elongate flexible catheter shaft **156**. Catheter shaft **156** is provided with a guidewire lumen **158**, together with at least a first and second inflation lumen **160** and **162**. In the illustrated embodiment, inflation lumen **160** is in communication with proximal balloon **150** and inflation lumen **162** is in communication with distal balloon **152**. In other

respects, the discussion in connection with the dual-lobed balloon of FIG. **15** is applicable to the dual balloon embodiment of FIG. **16**. In general, the dual balloon embodiment permits slightly more flexibility in terms of procedure, to the extent that it permits inflation of either the proximal or the distal balloon first, followed by inflation of the second balloon where clinically desirable.

Referring to FIGS. **17** and **18**, there is disclosed a therapeutic or diagnostic agent delivery embodiment of the catheters illustrated in FIGS. **15** and **16**. Referring to FIG. **17**, there is illustrated a dual-lobed delivery balloon catheter **170**. The catheter **170** comprises a dual-lobed balloon having a proximal lobe **172**, a distal lobe **174** and a central neck portion **176**. An outer perforated or permeable layer **178** extends at least from proximal lobe **172** to distal lobe **174** to entrap a space **180**. Space **180** is preferably annular, and is in communication with an infusion lumen **182** by way of one or more flow pathways **184**. In one embodiment, outer layer **178** comprises an elongate tubular sleeve, which is necked down at the proximal end of proximal lobe **172** and also at the distal end of distal lobe **174**.

The diameter of neck portion **176** is preferably at least somewhat smaller than the diameter of proximal lobe **172** and distal lobe **174**, to create space **180** for the accumulation of delivery media. A neck portion **176** which is inflatable to at least about 90% and preferably 95% or more of the diameter of adjacent lobes **172**, **174** permits delivery of media through the delivery zone yet minimizes the entrapped volume within space **180**. The inflated diameter of neck **176** can be limited by any of the inflation limiting techniques discussed above, such as one or more inflation limiting bands (not illustrated), cross linking, materials choice, wall thickness variations, and the like.

The inflated diameter of neck region **176** may alternatively be as small as permitted in view of the wall thickness of the balloon material, the wall thickness and diameter of the central guidewire lumen **184**, plus the space attributable to at least one flow passage **186** for communicating between the proximal lobe **172** and distal lobe **174** of the balloon.

Outer layer **178** may comprise any of a variety of materials, such as compliant or noncompliant materials well known in the drug delivery and balloon dilatation arts. For example, layer **178** may comprise PET, polyethylene, or other membrane materials well known in the art. Layer **178** may be a permeable membrane, such that medication or other media diffuses therethrough. Alternatively, layer **178** is preferably provided with a plurality of perforations **188** for permitting media to escape from the annular chamber **180** to the surrounding area.

The diameter and distribution of the perforations **188** can be modified depending upon the objective of the catheter, such as will be understood by those of skill in the art in view of the disclosure herein. For example, provision of delivery perforations within the range of from about 100 microns to about 300 microns in diameter will permit a slow weeping expression of fluid media at low delivery pressures. Alternatively, reducing the cross-sectional area of the perforations and/or increasing the delivery pressure can permit the media to penetrate through the elastic lamina layer and into the arterial wall. Port **188** diameter and distribution characteristics should also be selected taking into account the viscosity of any media to be delivered, and/or particle size if a particulate media is to be delivered.

One advantage of the configuration illustrated in FIGS. **17** and **18** is the ability to isolate an arterial delivery zone

in-between proximal lobe **172** and distal lobe **174**. Inflation of the dual lobes within an artery can be accomplished at relatively low pressures to place the balloons in contact with the arterial wall. Infusion of media into annular chamber **180** for expression through ports **188** may then be accomplished. Inflation pressure on the balloon can be increased, if an undesirably large quantity of media escapes downstream.

FIG. **18** is in all respects similar to FIG. **17** except for the use of two separately inflatable balloons. The details and operation of FIG. **18** will be apparent to those of skill in the art in view of the discussions in connection with FIGS. **15–17**.

Either of the drug delivery designs of FIGS. **17** and **18** may also incorporate a perfusion conduit, for permitting perfusion past the inflated balloon during a drug delivery period. Perfusion conduits such as those disclosed in U.S. Pat. No. 5,344,402 to Crocker, the disclosure of which is incorporated herein by reference, can be utilized.

Any of the hourglass type balloons of FIGS. **15–18** are particularly well suited for the implantation and/or sizing of vascular grafts. For example, an elongate tubular vascular graft can be positioned on the distal end of the catheter of FIG. **15** and transluminally advanced to the treatment site. As will be understood in the art, the treatment site may be a portion of a vessel having an aneurysm or other wall defect which is desirably spanned by the graft. The graft is preferably expanded by the balloon to a first diameter at the treatment site. The proximal and distal end zones of the graft are preferably expanded to a larger diameter so that they are seated against the vessel wall proximally and distally of the vessel wall defect. The balloon may then be deflated and withdrawn. If the embodiment of FIGS. **17** or **18** is used, the method may additionally include the step of expressing medication or other media at the treatment site. The balloons of the present invention may also be utilized for methods of sizing an already implanted graft and/or infusing medication or other media at the site of a previously implanted graft by positioning the balloon within the implanted graft and repeating the steps described above.

The present invention may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than the foregoing description. All changes which come within the meaning and range of equivalency of the claims are to be embraced within their scope.

What is claimed is:

1. A balloon catheter, comprising:

an elongate, flexible tubular body having proximal and distal ends;

an inflatable balloon on the distal end of the tubular body; and

an inflation lumen extending through the tubular body and communicating with the inflatable balloon;

wherein the balloon has a generally cylindrical first zone inflatable to a first diameter and a generally cylindrical second zone distal to the first zone and inflatable to a second, larger diameter.

2. A balloon catheter as in claim **1**, further comprising at least one expansion limiting band on the first zone.

* * * * *

[54] **PROCESS FOR PRODUCING POROUS PRODUCTS**

[75] Inventor: **Robert W. Gore**, Newark, Del.

[73] Assignee: **W. L. Gore & Associates, Inc.,** Newark, Del.

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Related U.S. Application Data

[63] Continuation of Ser. No. 39,753, May 21, 1970, abandoned.

[52] **U.S. Cl.**.............................. **264/288;** 264/175; 264/210 R; 264/290 R

[51] **Int. Cl.²**.. **B29D 7/24**

[58] **Field of Search** .... 260/29.6 F, 2.5; 264/191, 288, 290, 188, 184, 175

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*Primary Examiner*—Jay H. Woo
*Attorney, Agent, or Firm*—Finnegan, Henderson, Farabow & Garrett

[57] **ABSTRACT**

This invention provides a tetrafluoroethylene polymer in a porous form which has an amorphous content exceeding about 5% and which has a micro-structure characterized by nodes interconnected by fibrils. The material has high porosity and high strength. It can be used to produce all kinds of shaped articles such as films, tubes, rods, and continuous filaments. Laminations can be employed and impregnation and bonding can readily be used to produce a large variety of articles. Compressed articles of very high strength can also be produced from these porous forms.

24 Claims, 2 Drawing Figures

Fig. 1.
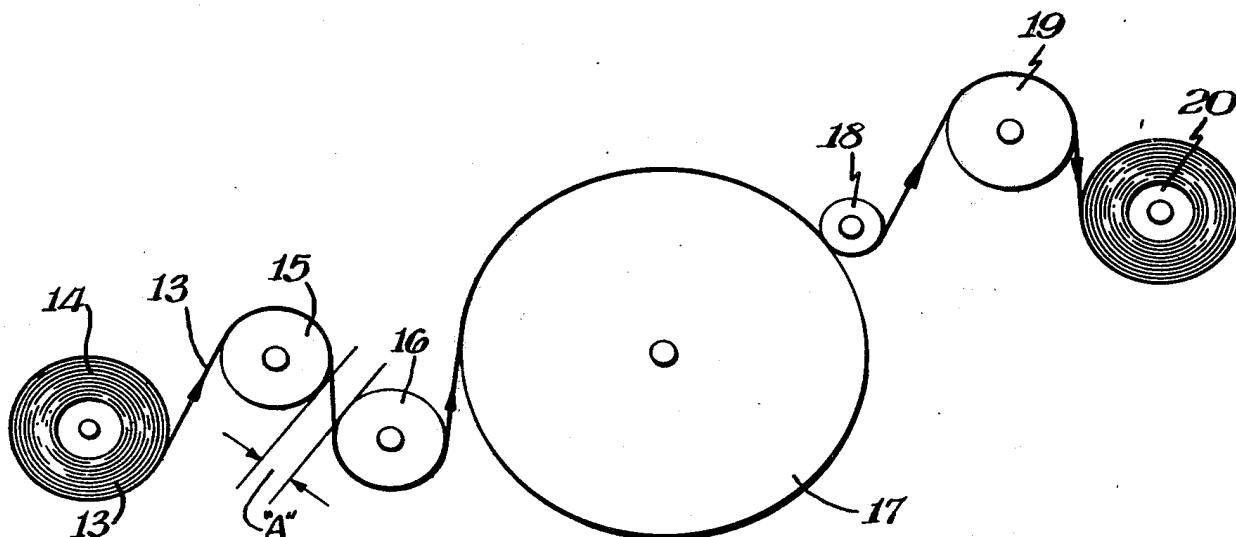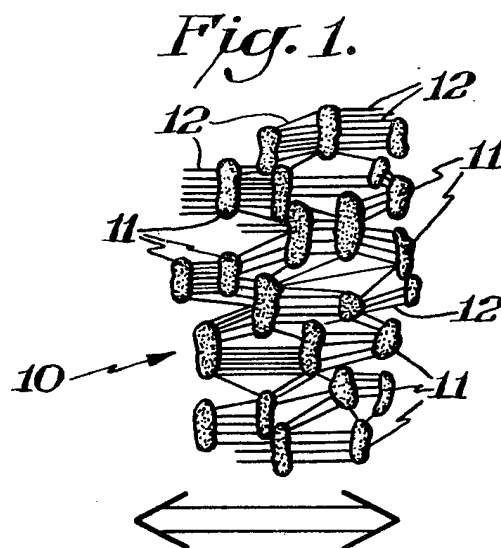
Direction of Uniaxial Expansion

Fig. 2.

1
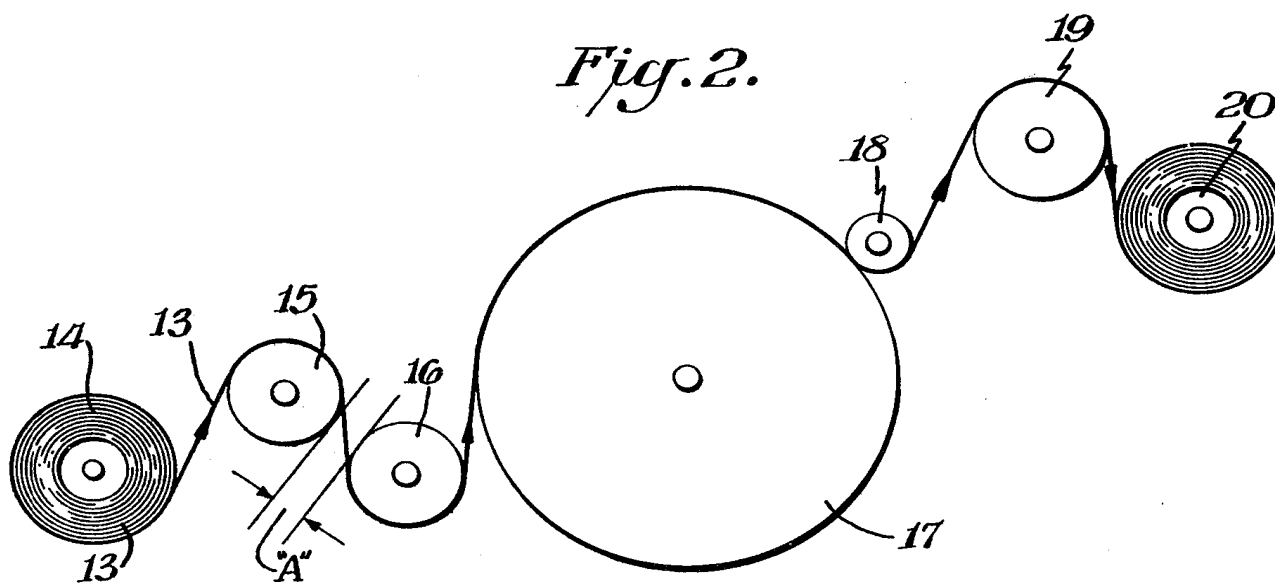
PROCESS FOR PRODUCING POROUS PRODUCTS

This is a continuation of application Ser. No. 39,753, filed May 21, 1970 now abandoned.

Tetrafluoroethylene polymers and, in particular, poly (tetrafluoroethylene) are gaining more and more uses because of their chemical inertness and desirable physical properties such as water-repellancy and electrical insulating abilities. In one very large area, the field of porous articles, their use has been substantially blocked by the very considerable difficulty of making an article porous and keeping it so and providing it with adequate strength. Complicated, expensive processes have been devised such as adding a filler to the polymer prior to shaping and then removing the filler after shaping, for example, by leaching it out of the shaped article with a solvent or by melting or burning it out. Not only are the process steps time consuming but the cost of such processes make them unattractive commercially.

Therefore, an objective of this invention is the provision of economical processes for producing highly porous materials from tetrafluoroethylene polymers. A further aim is to provide such processes which impart very high strengths to the resultant products. A still further purpose is providing the products themselves and, in particular, products from poly(tetrafluoroethylene) which are highly porous and have high strengths. Also, dense products of polytetrafluoroethylene are produced that have extremely high strength. These and other objectives appear hereinafter.

The invention described herein provides products of a tetrafluoroethylene polymer which have outstanding combinations of high porosity and high strength. In this regard they not only exceed previously available fluorocarbon polymeric products, but are unique among porous plastic materials. The porous structure produced by the processes of this invention is permeable and can be laminated, impregnated, and bonded with other materials to provide composite structures having novel and unique properties.

The objectives of this invention are accomplished by a process involving expanding paste-formed products of a tetrafluoroethylene polymer to make them both porous and stronger, and subsequently heat treating them to increase their strength further while retaining a porous structure. Paste-forming techniques are used to convert the polymer in paste form to a shaped article which is then expanded, after removing the lubricant, by stretching it in one or more directions; and while it is held in its stretched condition it is heated to at least 327°C after which it is cooled. The porosity that is produced by the expansion is retained for there is little or no coalescence or shrinking upon releasing the cooled, final article. The description and the examples below further describe the processes and the products of this invention.

Paste-forming of dispersion polymerized poly(tetrafluoroethylene) is well known commercially. Extrusions of various cross-sectional shapes such as tubes, rods and tapes are commonly obtained from a variety of tetrafluoroethylene resins, and other paste-forming operations such as calendering and molding are practiced commercially. The steps in paste-forming processes include mixing the resin with a lubricant such as odorless mineral spirits and carrying out forming steps in which the resin is subjected to shear, thus making the shaped articles cohesive. The lubricant is removed

from the extruded shape usually by drying. In usual practice this unsintered product is heated above the polymer's melting point, generally about 327°C., causing it to sinter or coalesce into an essentially impermeable structure. However, it is the unsintered product that is the precursor of the invention herein.

In this invention it has been found that such paste-formed, dried, unsintered shapes can be expanded by stretching them in one or more directions under certain conditions so that they become substantially much more porous and stronger. This phenomenon of expansion with increase in strength occurs with certain preferred tetrafluoroethylene resins and within preferred ranges of rate of stretching and preferred ranges of temperature. The preferred temperature range is from 35°C to 327°C. At the lower temperatures within this range it has been found that there is a maximum rate of expansion beyond which fracture occurs, as well as a lower limit beneath which fracture also occurs or where weak materials are obtained. The lower limit is of much more practical significance. At high temperatures within this range, only the lower limit of rate has been detected. The lower limit of expansion rates interact with temperature in a roughly logarithmic fashion, being much higher at higher temperatures. Most, but not all, of the desirable products of this invention are obtained when expansion is carried out at the higher temperatures within the range of 35°C to 327°C. The balance of orientation in the extruded shape also affects the relationship between the proper range of rates and temperature. It is found that some resins are much more suitable for the expansion process than others, since they can be processed over a wide range of rate and temperature and still produce useful products. The primary requisite of a suitable resin is a very high degree of crystallinity, preferably in the range of 98% or above, and correspondingly low amorphous content. It has been found that techniques for increasing the crystallinity, such as annealing at high temperatures just below the melt point, improve the performance of the resin in the expansion process. Copolymers of tetrafluoroethylene, which have defects in the crystalline structure that introduce a higher amorphous content, do not work as well in this invention as homopolymers. However, it is found, for example, that resins which contain less than 0.2% of hexafluoropropylene as a co-monomer can be made to work in this invention by going to very high rates of expansion at high temperatures just below the melt point.

The porous microstructure of the expanded material is affected by the temperature and the rate at which it is expanded. The structure consists of nodes interconnected by very small fibrils. In the case of uniaxial expansion the nodes are elongated, the longer axis of a mode being oriented perpendicular to the direction of expansion. The fibrils which interconnected the nodes are oriented parallel to the direction of expansion. These fibrils appear to be characteristically wide and thin in cross-section, the maximum width being equal to about 0.1 micron (1000 angstroms) which is the diameter of the crystalline particles. The minimum width may be one or two molecular diameters or in the range of 5 or 10 angstroms. The nodes may vary in size from about 400 microns to less than a micron, depending on the conditions used in the expansion. Products which have expanded at high temperatures and high rates have a more homogeneous structure, i.e. they have smaller, more closely spaced nodes and these

nodes are interconnected with a greater number of fibrils. These products are also found to have much greater strength.

It should be noted that during the expansion process a tremendous increase in strength is introduced into the structure, for while the porosity increases the strength actually increases, so there is often greater than a tenfold increase in strength of the polymeric matrix. In patent application Ser. No. 863,446, filed Oct. 3, 1969, a process is described for expanding unsintered poly(-tetrafluoroethylene) sheet, rods and shapes to give low density but low strength products. However, I have discovered that by performing the stretching at a very high rate, a surprising increase in strength is obtained. Although most materials fracture when subjected to a high rate of strain, highly crystalline poly(tetrafluoroethylene) withstands this treatment without breaking.

By definition, the tensile strength of a material is the maximum tensile stress, expressed in force per unit cross sectional area of the specimen, which the specimen will withstand without breaking (see, for example, The American Society for Testing and Materials. "1970 Annual Book of ASTM Standards - Part 24", at p. 41). For porous materials, the cross sectional area of solid polymer within the polymeric matrix is not the cross sectional area of the porous specimen, but is equivalent to the cross sectional area of the porous specimen multiplied by the fraction of solid polymer within that cross section. This fraction of solid polymer within the cross section is equivalent to the ratio of the specific gravity of the porous specimen itself divided by the specific gravity of the solid polymeric material which makes up the porous matrix. Thus, to compute matrix tensile strength of a porous specimen, one divides the maximum force required to break the sample by the cross sectional area of the porous sample, and then multiplies this quantity by the ratio of the specific gravity of the solid polymer divided by the specific gravity of the porous specimen. Equivalently, the matrix tensile strength is obtained by multiplying the tensile strength computed according to the above definition by the ratio of the specific gravities of the solid polymer to the porous product. In the examples which follow, both tensile strength and matrix tensile strength are shown, computed according to the above method, the lowest matrix strength measured being about 7300 p.s.i. In other words, the products shown herein all have matrix strengths of above about 7300 p.s.i.

When the expanded products are heated to above the lowest crystalline melting point of the poly(tetrafluoroethylene), disorder begins to occur in the geometric order of the crystallites and the crystallinity decreases, with concomitant increase in the amorphous content of the polymer, typically to 10% or more. These amorphous regions within the crystalline structure appear to greatly inhibit slippage along the crystalline axis of the crystallite and appear to lock fibrils and crystallites so that they resist slippage under stress. Therefore, the heat treatment may be considered an amorphous locking process. The important aspect of amorphous locking is that there be an increase in amorphous content, regardless of the crystallinity of the starting resins. Whatever the explanation, the heat treatment above 327°C. causes a surprising increase in strength, often doubling that of the unheat-treated material.

Because the upper melting range of poly(tetrafluoroethylene) polymer (as polymerized) is about 345°C, the heat treatment appears to be more effective above this temperature, although lower temperatures are equivalent if the exposure time is long enough. The optimum heat treating temperature is in the range of 350°C to 370°C and the heating periods required may range from about 5 seconds to about 1 hour. The microstructure of the expanded product is not substantially changed by the amorphous locking step. However, if the amorphous locking is carried out at too high a temperature for too long a time, the microstructure may become coarse as the nodes increase in size and the fibrils rupture, and in this case there is a noticeable deterioration in strength, but this presents no problem since one can very readily determine the optimum time and temperature for the given tetrafluoroethylene polymer being processed. Temperatures above about 390°C may cause this disintegration and loss of strength in less than one minute. In heat treating films it is essential that they be held so they cannot retract during the amorphous locking process. It is surprising that the expanded structures of this invention do not coalesce during the heat treatment to form high density products. If unexpanded films, having a density of about 1.5 gm/cm³ are so heated, they coalesce to form an essentially void-free material having a room temperature density of about 2.15 gm/cm³. Very little increase in density occurs when the products below about 1.00 gm/cm³ density are heated above the 327°C temperature.

The increase in strength of the polymer matrix is dependent upon the strength of the extruded material before expansion, the degree of crystallinity of the polymer, the rate and temperature at which the expansion is performed, and amorphous locking. When all these factors are employed to maximize the strength of the material, tensile strength of 10,000 psi and above, with porosity of 90% or more are obtained. In these cases the polymeric matrix has strengths in excess of 100,000 psi. In contrast, the maximum tensile strength of conventional extruded or molded poly(tetrafluoroethylene) after sintering is generally considered to be about 3,000 psi, and for conventional extruded and calendered poly(tetrafluoroethylene) tape which has been centered the maximum is about 5,100 psi.

Before describing examples of processes and products within this invention, a further description of the properties of expanded, amorphous-locked tetrafluoroethylene polymers will be helpful. As indicated above, some of the properties of these expanded, amorphously locked polymers are substantially different from the corresponding properties of conventional extruded or molded tetrafluoroethylene polymers. As a result of these differences, expanded, amorphously locked materials are useful in many applications where extruded or molded materials cannot be used.

These expanded, amorphous-locked materials have permeabilities to gases, and to liquids in some cases, which are much higher than the corresponding permeabilities of conventional molded or extruded poly(tetrafluoroethylene). The permeability to nitrogen of conventional poly(tetrafluoroethylene) film is reported in The Journal of Teflon, Jan.–Feb. 1970 (du Pont) at page 10 to be about 1×10^{-10} metric units.

In comparison, expanded, amorphous-locked films of this invention have permeabilities to nitrogen from about 1×10^{-8} to 1×10^{-1} metric units. These higher permeabilities are consistent with the lower densities and higher porosities of the expanded, amorphous-locked films, compared with conventional films. Fur-

thermore, by controlling the degree of expansion and the amorphous-locking conditions used, it is possible to make tetrafluoroethylene polymeric materials having any desired permeability within the range listed above. These permeability differences are due primarily to differences in pore sizes within the materials.

Also, permeabilities to liquids of the expanded, amorphous-locked materials described herein are higher, in an analogous way, than corresponding permeabilities to liquids of the conventional materials.

As a result of the ability of the expanded, amorphous-locked materials described herein to transmit fluids as described, these materials are useful as filtering membranes to separate solid materials from gases and from liquids. For optimum filtering rates, relatively low-permeability, small-pore size membranes are used to filter out small solid particles, and high-permeability, large-pore size membranes are used to filter out large solid particles.

Also, the expanded, amorphous-locked materials described herein are useful as semi-permeable membranes for separating wetting fluids from non-wetting fluids. For example, a gas-saturated membrane in contact with water and gas will transmit the gas, the wetting phase, as described above. But it will not transmit the water, the non-wetting phase, as long as the pressure in the water phase does not exceed the water entry pressure for that particular combination of membrane and fluids.

One factor which influences entry pressure of a non-wetting fluid into a porous material is the size of the pores. Since the size of the pores in the expanded, amorphous-locked materials described here can be and are controlled by the conditions used in the expanding and amorphous-locking operations, these materials are very useful, under a wide variety of conditions, as semi-permeable membranes.

The usefulness of the materials covered by this invention as filtering membranes for separating solids from fluids or as semi-permeable membranes for separating immiscible fluids from each other is enhanced by the following well-known highly desirable properties of tetrafluoroethylene polymeric materials: (1) outstanding chemical inertness and (2) resistance to undesirable physical changes over a wide temperature range.

The expanded, amorphous-locked material of this invention can be bonded to other materials and to itself much more readily than conventional poly(tetrafluoroethylene) products can. This is true because bonding agents are able to penetrate a significant distance into the pore network of expanded, amorphous-locked material, and, after hardening, they become locked in place. In contrast, there is negligible penetration of bonding agents into conventional tetrafluoroethylene polymers, and this, coupled with the general non-bonding nature of low energy surfaces make bonding difficult.

Certain other properties of expanded, amorphous-locked poly(tetrafluoroethylene) materials are better than the corresponding properties of conventional extruded or molded poly(tetrafluoroethylene) products, making the former materials more useful in many applications than the latter. The thermal conductivity of molded conventional poly(tetrafluoroethylene) is about 1.7 Btu/hr/sq.ft./°F/in. while that of the expanded, amorphous-locked polymer ranges from about one-tenth to about one-half that value. In line with this,

the more highly expanded materials of this invention have proven to be useful thermal insulators.

Similarly, expanded, amorphous-locked poly(tetrafluoroethylene) has shown an advantage over the conventional homopolymer as an electrical insulator in coaxial cables. The lower dielectric constant of the former, about 1.2 to 1.8, as compared with 2.2 for conventional polymer, permits smaller and lighter cables to be constructed by using the former. Many applications in which weight-saving (i.e. use of low density material) is an advantage can benefit by using the expanded, amorphous-locked polymers described herein in preference to conventional high density tetrafluoroethylene polymers.

This invention will be further understood by reference to the examples given below and to the drawings, all of which are given for illustrative purposes only and are not limitative, the drawings being:

FIG. 1 is a plan view of a section of an expanded, amorphously locked tetrafluoroethylene polymer as seen under a microscope; and

FIG. 2 is a diagrammatical view of an apparatus that may be used in the process of this invention to produce the expanded, amorphously-locked structures.

As shown in FIG. 1, the expanded, amorphously locked, porous material 10 of this invention comprises a large plurality of nodes 11 which are oriented perpendicularly to the direction in which the expansion was effected. These nodes, on the average about 50 microns in size and fairly irregular in shape, lie closely together and in many instances appear to touch at points. A given node is connected to adjacent or nearby nodes by fibrils 12 which vary in length from 5 to 500 microns depending upon the amount of expansion. While FIG. 1 shows a uniaxial expansion effect, it will be appreciated that with expansion biaxially and with expansion in all directions, similar fibril formation occurs in said directions with the production of spider-web-like or cross-linked configurations and attendant increases in strength. The porosity also increases as the voids or spaces between the polymeric nodes and fibrils become more numerous and larger in size.

The apparatus shown in FIG. 2 is described below in Example 5.

EXAMPLE 1

Expansion of Rods

A cylindrical rod of 5/32 inch diameter was made by extruding a paste of "Teflon" 6A resin containing 130 cc/lb. of mineral spirits as an extrusion aid, at a reduction ratio of 370 (the resin being obtainable from E.I. du Pont Nemours & Co., Inc.). The volatile extrusion aid was removed by drying, the resultant rod having a specific gravity of 1.63, a tensile strength of 531 psi, and an elongation of 183% (A.S.T.M. test method). The amorphous content of the "Teflon" 6A resin and the unsintered rod were determined using the infra-red method described by Moynihan, R. E. "IR Studies on Polytetrafluoroethylene", J. Am. Chem. Soc. 81, 1045–1050 (1959), and found to be 1.5%.

An apparatus was devised so that samples of the rod could be stretched various amounts at controlled rates and controlled temperatures. The apparatus consisted of two clamps for holding the rod, one clamp being held fixed within an oven while the other clamp was attached to a wire leading outside the oven to a rack-and-pinion pulling device driven by a variable speed

7 8

motor. After the sample had been expanded by stretching at the given controlled temperature, the oven temperature was raised to 370°C for 10 minutes while the samples were held clamped in their extended condi-

found to be 3.5%. While effective expansion was not obtained under the conditions of Example 1, at very much higher rates of expansion, expansion within this invention did occur:

TABLE 2

Temperature °F	Percent Stretch = 550		
	Rate of Stretch 5,000%/sec.	Rate of Stretch 10,000%/sec.	Rate of Stretch 40,000%/sec.
200	broke	broke	broke
400	broke	broke	68% porosity
600	broke	broke	68% porosity

tion. In some cases the samples broke during the expansion step and this is noted in tables below. The term "broke" refers to the fact that the particular sample being tested broke under the conditions given as an attempt was being made to stretch it to the final elongation given; the precise percentage of elongation at which the given sample broke is not given.

As can be seen in Table 1A, all samples were successfully expanded to a porosity of about 68% under the conditions of temperature and rate of stretch shown. Table 1B shows that samples at the lower values of temperature and rate could not be expanded by stretching 550%, while the rest of the samples were successfully expanded to a porosity of about 84%. Table 1C shows that only two samples were successfully expanded when the stretch was 1500%. These samples were obtained at the highest values of rate and temperature and had a porosity of about 96%.

Amorphously locking the porous products obtained applying the 40,000%/sec. rate of expansion was effected and the microstructures of the products conformed to such as shown in FIG. 1. The amorphous content after heat treatment at 370°C was 35%.

EXAMPLE 3

Expansion of Films

The following experiments were performed using a pantograph, which is a machine capable of stretching films biaxially or uniaxially over a range of rates and temperatures. The pantograph used in these experiments was capable of stretching 4 inch × 4 inch samples of film to 16 inch × 16 inch. The 4 inch × 4 inch film was gripped on each side by 13 actuated clamps, which moved apart uniformly on a scissor mechanism. The film was heated by hot air flow above and below.

A sample of film 6 inches wide, 0.036 inch thick, and

TABLES 1A, 1B and 1C

Table 1A: Percent Stretch = 200				
Temperature °F	Rate of Stretch 30%/sec.	Rate of Stretch 100%/sec.	Rate of Stretch 1000%/sec.	Rate of Stretch 5000%/sec.
200	67% porosity	67% porosity	67% porosity	66% porosity
400	66% ''	68% ''	67% ''	66% ''
600	66% ''	66% ''	67% ''	68% ''

Table 1B: Percent Stretch = 550				
Temperature °F	Rate of Stretch 30%/sec.	Rate of Stretch 100%/sec.	Rate of Stretch 1000%/sec.	Rate of Stretch 5000%/sec.
200	broke	broke	broke	broke
400	broke	84% porosity	85% porosity	85% porosity
600	broke	84% ''	84% ''	83% ''

Table 1C: Percent Stretch = 1500				
Temperature °F	Rate of Stretch 30%/sec.	Rate of Stretch 100%/sec.	Rate of Stretch 1000%/sec.	Rate of Stretch 5000%/sec.
200	broke	broke	broke	broke
400	broke	broke	broke	broke
600	broke	broke	96% porosity	96% porosity

This example illustrates that the most highly expanded products of this invention are obtained when the expansion is carried out at high temperatures and high rates of stretch. The amorphous content of these rods was found to be 24%.

EXAMPLE 2

Expansion of Rods

Rods 5/32 inch in diameter were manufactured under conditions similar to Example 1, except that "Teflon" 6C resin was used, this also being obtainable from said du Pont company. The amorphous content of the "Teflon" 6C resin and the unsintered rod were

of continuous length was produced by the paste extrusion process from "Teflon" 6A poly(tetrafluoroethylene) using 105 cc of mineral spirits per pound of resin as an extrusion aid. After removing the extrusion aid by drying, the unsintered film was found to have the following properties: specific gravity of 1.65, longitudinal tensile strength of 300 psi and transverse tensile strength of 250 psi.

Ex. 3(a): A 4 inch by 4 inch sample of this film was conditioned for approximately 4 minutes at 225°C in the pantograph and then stretched biaxially at a rate of 500%/sec. in each direction to a size of 16 inch × 16 inch. The temperature of the film was then raised to

370°C for 5 minutes while held clamped in the extended condition. The film was then cooled to ambient temperature and the following properties were found: specific gravity of 0.15, longitudinal tensile strength of 2,500 psi (a matrix tensile strength of 36,700 psi) and transverse tensile strength of 2,230 psi.

Ex. 3(b): A sample was prepared in all ways similar to Example 3(a) except that it was stretched in the pantograph at the lower rate of 55%/sec. The resulting film was still cohesive but was found to have weak areas, and a non-uniform appearance.

Ex. 3(c): A sample was prepared in all ways similar to Example 3(a) except that it was stretched at the even lower rate of 5%/sec. The film did not expand, but ruptured.

Ex. 3(d): A sample was prepared in all ways similar to Example 3(a) except that the temperature during expansion was 50°C. This film did not expand, but ruptured.

Ex. 3(e): A sample of paste-extruded film was taken before removal of the extrusion aid and calendered to a thickness of 0.0043 inch. The physical properties of the film were measured: specific gravity of 1.60; longitudinal tensile strength of 2,200 psi, and transverse tensile strength of 270 psi.

Samples of this film were stretch on the pantograph. The results are summarized in Table 3.

EXAMPLE 3(f)

Expanded Films Made By Biaxial Stretching

Another 4 inch × 4 inch sample of film of the type described in the second paragraph of Example 3 above was stretched in the pantograph machine. In this case, the film was stretched simultaneously in two directions at right angles to each other, 100% in each direction. Thus, the surface area of the stretched film was four times the surface area of the original film.

The film temperature was about 300°C during the stretching operation. Linear stretching rates of about 400% per second in each dimension were used.

With the expanded film still in tension (stretcher clamps still holding the stretched film), hot air was circulated over the film such that the film temperature was about 360°C for five minutes. This caused amorphous locking within the film.

Finally, with the stretcher clamps still holding the film, the film was cooled rapidly to room temperature by blowing cold air against it. The cooled film, which was then removed from the clamps, was the desired expanded, amorphous-locked film.

Properties of the original unexpanded film and of the final expanded, amorphous-locked film, which show the advantage of this invention, are listed below.

TABLE 3

Temperature °C	Expansion Rate In Longitudinal Direction (%/sec.)	Example 3(e) Expansion Rate In Transverse Direction (%/sec.)	Result
225	500	500	Ruptured
225	500	0	Long. Tensile = 3900 psi (a matrix tensile strength of 12,800 psi) Trans. Tensile = 1150 psi Spec. Gravity = 0.70
225	0	500	Ruptured
50	500	500	Ruptured
50	500	0	Ruptured
50	0	500	Long. Tensile = 2400 psi (a matrix tensile strength of 7,360 psi) Trans. Tensile = 2700 psi Spec. Gravity — 0.75
225	5	5	Ruptured
225	5	0	"
225	0	5	"
50	5	5	"
50	5	0	"
50	0	5	"

From the tabulated results, it can be seen that the film responded differently depending on which axis was stretched but that at the low rates rupture occurred irrespective of the direction of expansion.

TABLE 4

Property	Original Unexpanded Film	Expanded Amorphous-Locked Film	
Film Length, relative units	1	1.9	
Film Width, relative units	1	2.0	
Film Thickness, mils	36.0	31.5	
Specific Gravity	1.65	0.45	
Long. Tensile Strength, psi	300	1900	(matrix tensile strength of 9,290 psi)
Transverse Tensile Strength, psi	250	1760	
Permeability to air, metric units	4×10^{-5}	6×10^{-3}	

11
EXAMPLE 4
Expansion of Filled Films

The "Teflon" 6A resin, identified above, was blended with a commercially available asbestos powder in proportion of four parts by weight resin to one part asbestos. The mixture was lubricated with 115 cc of odorless mineral spirits per pound of mixture and extruded into a film 6 inches wide, 0.036 inch thick, and of continuous length. The fil, was then calendered to 0.008 inch thickness and the extrusion aid removed by drying. The properties were measured and found to be as follows: specific gravity of 1.44, longitudinal tensile strength of 1,000 psi; and transverse tensile strength of 205 psi.

A 4 inch × 4 inch sample was mounted in the pantograph described above and stretched at a rate of 500%/sec. at a temperature of 225°C. and to three times its original length in the longitudinal direction while no stretch was applied in the transverse direction. A sample of the film was tested and found to have the following properties: specific gravity of 0.82, longitudinal tensile strength of 1500 psi, and transverse tensile strength of 145 psi. The remainder of the sample was placed in clamps to restrain it from shrinking, heated to 370°C for 5 minutes, and then cooled to room temperature. The following properties were measured on this sample: specific gravity of 0.95, longitudinal tensile strength of 2,900 psi, and transverse tensile strength of 750 psi.

The heat treating of the film substantially increased

12

be driven faster than roll 15 so that the film is stretched in the gap A between the rolls making the film expand. The difference in speed determines the amount of stretch and thus the amount of expansion. For example, when roll 16 is driven twice as fast as roll 15, the film is expanded approximately 100% because, unlike other films, the unsintered poly(tetrafluoroethylene) film changes very little in thickness or width and the length increases by 100%. The increase in volume is due to an increase of porosity and a corresponding decrease of specific gravity. The relative positions of rolls 15 and 16 are adjustable so that the gap A between them can be varied. This allows one to control the rate of expansion. For example, when the gap distance is halved, the rate of expansion is doubled. It should be noted that the rate of expansion is also effected by the rate at which film is fed into the machine. Roll 16 is maintained at the same temperature as roll 15. Expanded film leaves roll 16 and goes onto roll 17 (running at the same peripheral speed) which is hot, and where the film is heated to approximately 370°C so that amorphous locking will occur. The residence time of film on this roll is controlled by the position of roll 18, which can be moved around the periphery of roll 17. Roll 19 is water cooled to reduce the temperature of the film as it passes thereover before being wound up on roll 20. Thus, with this machine one is able to control the three important variables necessary for expanding tetrafluoroethylene polymer film, i.e. the temperature, the rate of expansion, and the amount of expansion.

Three runs on this apparatus are given in Table 5.

TABLE 5

Resin:	"Fluon" CD-1 (obtainable) from Imperial Chemical Industries, Ltd.)	"Teflon" 6A	"Teflon" 6A preheated 3 hrs. at 300°C. prior to paste extrusion
Properties of starting film:	(a)	(b)	(c)
Thickness of Film	0.0050"	0.0050"	0.0050"
Density, gm/cm³	1.47	1.52	1.54
Longitudinal tensile, psi	1600	1900	2650
Transverse tensile, psi	200	250	350
Processing conditions:			
Tape feed rates:			
roll 14 to roll 15	30 ft./min.	30 ft./min.	30 ft./min.
Temp., Rolls 15 and 16	300°C.	300°C.	300°C.
Roll speed ratio:			
roll 15:roll 16	1:2.87	1:2.87	1:2.87
Calculated rate based on 3" stretch length	574%/sec.	574%/sec.	574%/sec.
Temp. for roll 17	370°C.	370°C.	370°C.
Dwell time on roll 17	3 sec.	3 sec.	3 sec.
Properties of Final Film:			
Thickness	0.0047"	0.0048"	0.0046"
Density, gm/cm³	0.66	0.67	0.73
Long. Tensile, psi	2850 (matrix tensile strength of 9,500 psi)	4000 (matrix tensile strength of 13,100 psi)	8950 (matrix tensile strength of 27,000 psi)
Transverse tensile, psi	850	1050	1300

its tensile strength as can be seen from the above values, and had a very little effect on specific gravity.

EXAMPLE 5

Manufacture of Continuous Lengths of Porous Film

A machine was constructed for manufacturing long lengths of expanded film. As can be seen in FIG. 2, unsintered film 13 from the paste extrusion process is fed to the machine from roll 14 onto heated roll 15 where the film is preheated to the temperature at which it will be expanded. Rolls 15 and 16 are of the same diameter and are connected through a gear box so their relative rates of rotation can be changed. Roll 16 can

EXAMPLE 6

Expanded Films Made by Vacuum Forming

The vacuum-forming process and the product made thereby, which are described below, are another example of this invention.

Again, the starting material was extruded, unsintered "Teflon" 6A poly(tetrafluoroethylene) film in this case with a specific gravity of 1.50 and a thickness of 3.9 mils. A rectangular section of this tape was placed in a vacuum-forming device, the temperature of which could be raised with an electric heater or lowered with a stream of cold air. The film was clamped in place, and

the temperature of the assembly was raised to about 300°C. Then the pressure in the expansion chamber was reduced rapidly causing the film to be stretched very rapidly to about three times its original area into the shape of a bowl.

Without releasing the vacuum, the temperature of the assembly was raised to about 350°C. where it was held for about 10 minutes. Then the assembly was cooled as rapidly as possible by blowing with cold air, and finally the vacuum was released and the expanded, amorphous-locked film was removed from the vacuum-forming device.

Properties of the original film and the expanded, amorphous-locked film, made as described above, are listed below.

TABLE 6

Property	Original Unexpanded Film	Expanded, Amorphous-Locked Film
Film area, relative units	1.0	2.1
Film thickness, mils	3.9	3.7
Specific Gravity	1.50	0.75
Long. tensile strength, psi	1800	4100
Transverse tensile strength, psi	240	1400

The greatly enhanced strengths and porosity that are achieved by this invention are clearly shown in the above table.

EXAMPLE 7

Expanded, Amorphous-Locked Film Made By Stretching Using A Molding Device

A section of extruded, unsintered poly(tetrafluoro-ethylene) film was fastened to the female member of a molding device, and the assembly was heated to 275°C. by circulating hot air over it. Then the male member, which was bowl shaped, was rapidly forced against the film causing it to stretch to about three times its original surface area without crushing the stretched film between the members of the molding device.

With the film still held in place, the entire assembly was heated to about 340°C. for 15 minutes, after which it was cooled to room temperature. Then clamps holding the film were released, and the desired expanded, amorphous-locked film was obtained.

Properties of the original film and the final expanded amorphous-locked film are listed below:

TABLE 7

Property	Original Extruded, Unsintered Film	Expanded, Sintered Film
Surface area, relative units	1.0	2.6
Thickness, mils	15	12
Specific Gravity	1.50	0.72
Thermal conductivity, Btu/hr/sq.ft/°F./in.	1.5	0.5
Permeability to kerosene, metric units	1.9×10^{-7}	28×10^{-7}

EXAMPLE 8

Expanded Tube Made By Blowing

The starting material in this example was extruded, unsintered "Teflon" 6A poly(tetrafluoroethylene) tubing having an outside diameter of 020 inch and a wall thickness of 30 mils.

A 15 inch long section of this tubing was plugged off at one end, and the other end was clamped to a steel tube, which, in turn, was connected to a source of compressed gas.

The tubing was placed in an air oven, and the assembly was heated to about 300°C. Compressed gas was admitted to the tubing in such a way that the diameter of the tube was increased in about 2 seconds from the original 0.20 inch to about 0.60 inch. Then, with pressure maintained in the tubing so that no collapse took place, the temperature of the assembly was raised to about 360°C. and held there for about 5 minutes. While still maintaining pressure to prevent tubing collapse, the assembly was colled rapidly using a stream of cold air, yielding the desired expanded, amorphous-locked tubing.

Properties of the original tubing and the expanded, amorphous-locked tubing are as follows:

TABLE 8

Property	Original Unexpanded Tubing	Expanded, Amorphous-Locked Tubing
Length, relative units	1.0	0.8
Outside diameter, inches	0.20	0.56
Wall thickness, mils	30	24
Specific gravity of tubing walls	1.50	0.75
Air permeability of tubing walls, metric units	2×10^{-5}	1×10^{-3}

The above expanded, amorphous-locked tubing was useful as a filtering membrane for separating solids from fluids due to its high permeability.

15

EXAMPLE 9

Expanded, Amorphously Locked, Laminated Film Made From Two Layers of Expanded Film

Using the tape expanding machine illustrated in FIG. 2 but with the amorphous-locking roll **17** set at 300°C., a sample of expanded, "Teflon" **6A** poly(tetrafluoroethlyene) film was made. This film had a specific gravity of 0.60 longitudinal tensile strength of 1900 psi (a matrix tensile strength of 7,300 psi), transverse tensile strength of 110 psi, and a thickness of 3.5 mils.

Two sections of this film, at right angles to each other and one on top of the other, were clamped to a rigid frame which secured all four edges of the sandwich and pushed one film lightly against the other over the whole area of contact. This assembly was given an amorphous-locking treatment by heating it about 370°C. for 7 minutes. Then the whole assembly was rapidly cooled with a stream of cold air, and clamps were released yielding the desired one-piece laminated film.

The tensile strength of the expanded, amorphous-locked laminate was 4300 psi in each direction. Its thickness was 6.4 mils.

EXAMPLE 10

Expanded, Amorphous-Locked Film As A Filtering Membrane Or A Semi-Permeable Membrane

An extruded, calendered, unsintered "Teflon" **6A** poly (tetrafluoroethylene) film was made using the known conventional procedure described above. This film was expanded and amorphously locked using the machine of FIG. 2 and the process of this invention described herein. Expansion was carried out at a temperature of about 300°C., and amorphous locking at about 370°C. Properties of the original film and the expanded, amorphous-locked film are listed below:

TABLE 9

Property	Original Unexpanded, Unsintered Film	Expanded Sintered Film
Thickness, mils	4.0	3.5
Surface area*, relative units	1.0	2.8
Specific Gravity	1.46	0.60
Permeability to air, metric units	1.0×10^{-4}	0.032
Permeability to kerosene, metric units	7.0×10^{-7}	2.3×10^{-4}

*Length × width

Smoke-containing air was filtered through a sample of the expanded, amorphous-locked film described above. It was observed that the filtered air was clean, and the filtering rate was relatively high. A similar effort to filter smoke-containing air using a sample of the unexpanded, unsintered film described above was unsuccessful because the filtering rate was too low.

Similarly, samples of the expanded, amorphous-locked film described above were used to filter solids from suspensions of the solids in various organic liquids. Again, good separations were obtained, and filtering rates were reasonably high. However, similar attempts using samples of the unexpanded, unsintered film described above again were unsuccessful because of extremely low filtering rates.

16

When an effort was made to flow water through the (air-saturated) expanded, amorphous-locked film described above using 5 psi flowing pressure, no flow occurred. However, when the applied flowing pressure exceeded 10 psi, the water entry pressure of the gas-saturated membrane, flow started, and thereafter flow of water through the membrane was quite similar to the flow of wetting organic liquids. This membrane was found to be useful in separating solids from dispersions of the solids in water.

A sample of the expanded, amorphous-locked film described above was fitted into the cone of a filtering funnel, and a mixture of kerosene and water was poured into the funnel. The kerosene flowed through the film at a reasonably rapid rate, but no water penetrated the film since the pressure in the water phase was lower than the water entry pressure into either the gas-saturated or the kerosene-saturated film. Thus, the expanded, amorphously locked film was found to be an effective semipermeable membrane useful in separating fluids that wet tetrafluoroethylene polymers from non-wetting fluids. Similar attempts to use the unexpanded, unsintered film described above as a semipermeable membrane were unsuccessful because of the extremely low flow rates involved.

EXAMPLE 11

Expanded, Amorphously Locked Film Impregnated With Poly(Methyl Methacrylate)

A part of the expanded, amorphous-locked film prepared as described in Example 10 was painted with a freshly made solution of 1% of polymerization initiator 2,2' azo-bis (2-methylpropionitrile) in methyl methacrylate). The solution was rapidly imbibed into the expanded, amorphously locked film. Any excess solution not so imbibed was wiped from the surface of the film.

Then the impregnated film was warmed, causing the methyl methacrylate to polymerize within the pores of the expanded, amorphous-locked film, thus yielding a film having pores filled with poly(methyl methacrylate).

The comparison shown below of the properties of conventional extruded, calendered, unsintered poly(tetrafluoroethylene) film with those of the expanded, amorphous-locked, film impregnated with the methacrylate polymer shows clearly the greater dimensional stability of the impregnated film without significant increase in the coefficient of friction. These properties make impregnated materials of the type described here particularly useful as bearing materials. The substantially lower cost of the impregnated material, as compared with the conventional homopolymer or copolymers, is a further benefit of this invention.

TABLE 10A

Property	Conventional Unexpanded, Unsintered Film	Expanded, Amorphous-Locked, Impregnated Film
Deformation, 150 psi Compressive Stress at 77°F,%	2.7	0.7
Coefficient of Friction against Glass	0.20	0.21

In further impregnation experiments, a piece of expanded, amorphous-locked poly(tetrafluoroethylene) film made as described in Example 10 was impregnated with a low viscosity epoxy resin, ER LA 2256, a product of and obtainable from Union Carbide Corporation. A second piece of the film was impregnated with a solution of metaphenylenediamine in methyl ethyl ketone. When the ketone had evaporated, the two pieces, with the longitudinal dimension of one coinciding with the transverse dimension of the other, were placed in contact with each other, and the assembly was heated at about 300°F for about 3 hours.

The two pieces were firmly bonded by the hardened epoxy resin. Properties of the laminate were as follows:

to make up a core separating the inner conductor of the coaxial cable from an outer metallic braided shield. An outer jacket constructed of conventional poly(tetrafluoroethylene) covered the shield. The characteristic impedance of the cable was 100 ohms.

A second coaxial cable having an impedance of 100 ohms was constructed, in this case using conventional, unexpanded tape to construct the core. After sintering, the density of the poly(tetrafluoroethylene) core was about 2.15 gms/cc.

Because of the lower dielectric constant of expanded, amorphous-locked poly(tetrafluoroethylene) over that of the conventional polymer, a smaller, lighter cable was obtained when expanded, amorphous-locked tape was used. This is shown in detail in the following table.

TABLE 11

Item	A 100 Ohm Impedance Cable Made Using A Core Of Conventional Polymer	B 100 Ohm Impedance Cable Made Using A Core Of Expanded, Amorphously Locked Polymer
Conductor Weight, g/ft	0.064	0.064
Polymer Insulation, g/ft	3.890	0.464
Braided Metal Shield, g/ft	2.700	1.898
Polymer Jacket, g/ft	0.855	0.569
Core Diameter, in.	0.110	0.065
Outer Diameter of Cable, Inch.	0.140	0.095
Total Cable Weight, g/ft	7.509	2.995

TABLE 10B

Property	Expanded, Amorphous-Locked Film	Laminate
Longitudinal tensile strength, psi	8,100	8,800
Transverse tensile strength, psi	1,500	8,800
Deformation, 100 psi Compressive Stress at 77°F., %	13	1.2
Coefficient of Friction Against Glass	0.14	0.14

EXAMPLE 12

Use Of Expanded, Amorphous-Locked Tape As Core Of A Coaxial Cable

Expanded, amorphous-locked tape was made following the procedure described in Example 10. Two such tapes were made, both having a specific gravity of about 0.66, one having a thickness of 2.5 mils, the other, 10 mils. Alternate wraps of (1) the thinner tape, (2) the thicker tape, and (3) the thinner tape were used

The data listed above show that the use of expanded, amorphous-locked polymer in B rather than conventional polymer in A as the core in this cable led to a 60% reduction in weight and a 32% reduction in size of the cable.

EXAMPLE 13

Films Which Are Very Greatly Expanded And Then Amorphous-Locked

Unsintered, extruded, calendered poly(tetrafluoroethylene) film was made using the known conventional procedure described in earlier examples. This film had a thickness of 4.0 mils.

Using the apparatus of FIG. 2 and above procedures, parts of this film were expanded without amorphous-locking using a step-wise procedure. The machine was set at 190% expansion for each of the expansion runs. Then samples of the expanded films were passed through the machine to lock them amorphously at 370°C. without further expansion. The steps followed in this work are explained in the following diagram:

Original, unsintered, calendered film
   | expanded 190% without
   | amorphous locking   Sample (A) amorphously

-continued

```
                                          locked at 370°C.
1 pass material (A) ─────────────────────────► Product 1
    again expanded, 190%
    without amorphous
    locking                                Sample (B) amorphously
                                          locked at 370°C.
2 pass material (B) ─────────────────────────► Product 2
    again expanded 190% with-
    out amorphous locking                 Sample (C) amorphously
                                          locked at 370°C.
3 pass material (C) ─────────────────────────► Product 3
    again expanded 190% with-
    out amorphous locking                 Sample (D) amorphously
                                          locked at 370°C.
4 pass material (D) ─────────────────────────► Product 4
```

Properties of the films produced as described above are listed below:

TABLE 12

Film Identity	Expansion, %	Thickness, mils	Specific gravity
Original film	none	4.0	1.50
Product 1	190	3.8	0.50
Product 2	190 × 2	3.8	0.27
Product 3	190 × 3	3.1	0.18
Product 4	190 × 4	2.8	0.17

Film Identity	Porosity, %	Bulk Long. Tensile Strength, psi	Long. tensile strength of polymeric matrix, psi
Original film	35	1,640	2,600
Product 1	78	2,900	14,000
Product 2	88	2,420	30,000
Product 3	92	2,400	30,000
Product 4	93	2,400	34,000

EXAMPLE 14

"Teflon" 6A polymer was heated for 3 hours at 300°C., cooled, blended with 80 cc of refined kerosene per pound of polymer, and extruded into a film 6 inches wide, 0.030 inch thick, using a reduction ratio of about 100 (reduction ratio = cross-section area of extrusion cylinder divided by the cross-section of the extrudate). The extruded film was then passed through successive sets of rolls, each heated to about 80°C., and reduced in thickness from 0.030 inch to 0.002 inch. This film was dried to remove the kerosene and passed through the apparatus of FIG. 2 at a rate of 100 ft./min. over roll 15, with rolls 15 and 16 heated to 320°C. and adjusted with their outer peripheries as close together as possible without crushing the 0.002 inch film between them. Roll 16 (and 17, 18, 19) was rotated at a peripheral speed seven times greater than roll 15, thus stretching the film about sevenfold. The film was passed over roll 17 at 370°C. and wound up on take-up 20. Rolls 15, 16, 17, 18 and 19 were then adjusted to the same peripheral speed of 30 ft./min., rolls 15, 16 and 17 adjusted to 370°C., and the stretched film passed through the appa-

ratus under these conditions in order to accomplish an adequate heat treating. The properties of the film were as follows:

Thickness	.0019"
Density gm/cm³	.23
Longitudinal tensile psi	12,200
Longitudinal tensile of polymer matrix	$\frac{2.2 \text{ gm/cc}}{.23 \text{ gm/cc}} \times 12,000 = 117,000 \text{ psi}$

EXAMPLE 15

Amorphous Content of Polymer

A sample of film was prepared as in Example 14 except that it was rolled to a thickness of 0.004 inch. This film was then expanded using the same process as in Example 5 except that roll 17 was not heated. Heat treatments were carried out on samples of this film at 335°C., 350°C., and 390°C. for various lengths of time. The amorphous content of the polymer was determined at each stage in the process using the infra-red method described by Moynihan, R. E. "IR Studies on Polytetrafluoroethylene", J. Am. Chem. Soc. 81, 1045–1050 (1959). The properties of the films were as follows:

TABLE 13

	Longitudinal Tensile Strength Matrix Tensile Strength	% Amorphous	Density, gm/cm³
"Teflon" 6A powder, heat treated		1.5%	
Extruded, dried .004" film	2650	1.5%	1.5
Expanded not heat-treated	4200/14,200	1.5%	.68
Heated to 335°C:			
1 second	5580/18,500	2.5%	.69
10 seconds	5630/18,400	3%	.70
50 seconds	6020/19,700	4%	.70
480 seconds	7540/24,600	5%	.70
Heated to 350°C:			

TABLE 13-continued

	Longitudinal Tensile Strength Matrix Tensile Strength	% Amorphous	Density, gm/cm³
1 second	7630/24,700	10%	.70
3 seconds	7670/24,900	10%	.70
10 seconds	7820/25,200	15%	.70
20 seconds	7830/24,900	25%	.70
50 seconds	8360/26,400	30%	.70
100 seconds	8610/27,100	33%	.70
480 seconds	8900/27,900	35%	.70
Heated to 390°C:			
1 second	7500/23,500	25%	.71
3 seconds	7960/23,900	35%	.73
10 seconds	7830/23,400	38%	.73
20 seconds	7270/20,300	40%	.78
50 seconds	6560/16,800	40%	.85
90 seconds	disintegrated		

EXAMPLE 16

High Strength, Low Porosity Films

A sample of expanded but not heat-treated film from Example 15 was placed in a platen press, compressed at 300 psi and while held compressed, the platens were heated to 350°C. and then cooled rapidly. The longitudinal tensile strength of the resulting film was 24,000 psi and the density 2.10 gms/cm³, about 3% porosity. Therefore, it is possible to produce very high strength, high density products by compressing the expanded material during the amorphous-locking step. The fibril-node structure is preserved even though the porosity is reduced to about 3%. With higher pressures it is possible to further reduce the porosity and still preserve the very high strength of the material.

A second sample of the expanded film from Example 15 which had been heat treated at 350°C. for 8 minutes was placed in the press at room temperature and compressed at 1500 psi for several minutes. The film was clear and transparent. Its density was 2.05 gms/cm³ and longitudinal tensile strength was 21,000 psi. Therefore, it is feasible to compress the porous structure of the product and still preserve the high strength of the bulk polymer.

The foregoing examples clearly show the desirable effect of expansion and amorphous-locking on the tensile strength and density characteristics of the products, and also that the high tensile strength is retained when the porous structure is compressed.

The formation of the porous material by this invention can be accomplished using poly(tetrafluoroethylene) or copolymers of tetrafluoroethylene with other monomers. Such monomers are ethylene, chlorotrifluoroethylene, or fluorinated propylenes, such as hexafluoropropylene. These monomers are used only in very small amounts since it is preferred to use the homopolymer for the reason that it presents the optimum crystalline/amorphous structure for the process and the products of this invention. Thus, amounts of the comonomers are generally less than 0.2% and it is highly preferred to use poly(tetrafluoroethylene). While the above examples show the use of asbestos as a filler, it is to be appreciated that a wide variety of fillers can be incorporated such as carbon black, pigments of various kinds as well as inorganic materials such as mica, silica, titanium dioxide, glass, potassium titanate, and the like. Further, fluids may be used which include dielectric fluids or materials such as the polysiloxane materials shown in U.S. Pat. No. 3,278,673.

While the invention has been disclosed herein in connection with certain embodiments and certain structural and procedural details, it is clear that changes, modifications or equivalents can be used by those skilled in the art; accordingly, such changes within the principles of the invention are intended to be included within the scope of the claims below.

What is claimed is:

1. A process for the production of a porous article of manufacture of a polymer of tetrafluoroethylene which process comprises expanding a shaped article consisting essentially of highly crystalline poly(tetrafluoroethylene) made by a paste-forming extrusion technique, after removal of lubricant, by stretching said unsintered shaped article at a rate exceeding about 10% per second and maintaining said shaped article at a temperature between about 35°C. and the crystalline melt point of said tetrafluoroethylene polymer during said stretching.

2. The process of claim 1 in which the rate of stretch is about 30% per second.

3. The process of claim 1 in which the rate of stretch is about 100% per second.

4. The process of claim 1 in which the rate of stretch is about 500% per second.

5. The process of claim 1 in which the rate of stretch is about 1000% per second.

6. The process of claim 1 in which the rate of stretch is about 5000% per second.

7. The process of claim 1 in which the rate of stretch is about 10,000% per second.

8. The process of claim 1 in which the rate of stretch is about 40,000% per second.

9. A process in accordance with claim 1 in which said shaped article has an amorphous content not exceeding about 3.5%.

10. A process in accordance with claim 1 in which said expanding is effected by clamping said shaped article and rapidly forming a vacuum on one side of said article to rapidly stretch said shaped article.

11. A process in accordance with claim 1 in which said expanding is effected in only one direction.

12. A process in accordance with claim 1 in which said expanding is effected biaxially.

13. A process in accordance with claim 1 in which said expanding produces a porosity of about 40% to about 97% in said resultant, porous stretched article.

14. A process according to claim 1 including the step of compressing the resultant porous article.

23

15. The process of claim **1** in which said shaped article is expanded by rapidly creating a pressure differential across said shaped article to cause said shaped article to stretch.

16. The process of claim **1** in which the expanding step is effected at a temperature above about 93°C.

17. The process of claim **1** in which the shaped article is expanded such that its final length in the direction of expansion is greater than about twice the original length.

18. The process of claim **17** in which said final length is greater than about three times the original length.

19. The process of claim **17** in which said final length is greater than about five times the original length.

24

20. The process of claim **17** in which said final length is greater than about seven times the original length.

21. The process of claim **17** in which said final length is about fifteen times the original length.

22. The process of claim **17** in which said final length is greater than about 24 times the original length.

23. A process in accordance with claim **1** which includes the subsequent step of heating the stretched-shaped article to a temperature above the crystalline melting temperature of said polymer.

24. The process of claim **23** in which said heating produces in said stretched-shaped article an increase in amorphous content exceeding about 1%.

* * * * *

Disclaimer

3,953,566.—*Robert W. Gore,* Newark, Del. PROCESS FOR PRODUCING PO-
ROUS PRODUCTS. Patent dated Apr. 27, 1976. Disclaimer filed Apr.
25, 1984, by the assignee, *Gore Enterprise Holdings, Inc.*

Hereby enters this disclaimer to claims 1 and 17 of said patent.

[*Official Gazette January 1, 1985.*]

1

2

3,376,238
PROCESS FOR FORMING CROSSLINKED ORIENTED, MICROPOROUS POLYOLEFIN FILM

Razmic S. Gregorian, 8460 Piney Branch Court, Silver Spring, Md. 20901, and Charles C. Kirk, 2808 Johns Hopkins Road, Laurel, Md. 20810
No Drawing. Continuation-in-part of application Ser. No. 337,186, Jan. 13, 1964. This application May 19, 1966, Ser. No. 551,248
4 Claims. (Cl. 260—2.5)

ABSTRACT OF THE DISCLOSURE

A process for forming crosslinked biaxially oriented, microporous, polyolefin-containing film comprising admixing said polyolefin with a finely divided pore forming solid, heating the mixture above the melting point of the polyolefin to shape same in the form of film, crosslinking the shaped mixture by either adding an organic compound capable of generating free-radicals or employing ionizing irradiation and thereafter extracting the pore forming solid at a temperature below the degradation temperature of the crosslinked polyolefin. The polyolefin film can, if desired, be biaxially oriented either after the crosslinking step or after the extraction of the pore forming solid.

This application is a continuation-in-part of our prior copending application Ser. No. 337,186 filed Jan. 13, 1964 now abandoned.

This invention relates to a novel and useful composition of matter, a process utilizing the composition and the product resulting from the process. More particularly, it is directed to filled polyolefin containing compositions, e.g. polyethylene, polypropylene and copolymers of ethylene and vinyl monomers, a process employing said compositions and the microporous product resulting therefrom.

It is known in the art to render thermoplastic polymers, microporous by including therein a pore-forming solid which is subsequently removed. The pore-forming solid is extracted at low temperatures which do not cause physical or chemical changes, e.g. swelling of the polymer. This necessitates prolonged extraction periods and adds considerably to the production cost of forming microporous polymers. In addition, the resulting microporous thermoplastic resin has a low melting or softening temperature and low resistance to organic solvents. For example, low density polyethylene softens and loses its shape in boiling water. Furthermore, said polyethylene is soluble in xylene and similar organic solvents particularly at elevated temperatures. Such drawbacks greatly deter forming microporous material from polyethylene since its commercial usefulness is curtailed by such short comings.

One object of this invention is to provide a process for greatly increasing the physical and chemical resistance of microporous polyolefins to organic solvents.

An additional object of the present invention is to devise a process whereby extraction of the pore-forming solids can be carried out at an increased rate at elevated temperatures. Yet another object is to provide a novel process for decreasing the solubility of microporous polyolefins in organic solvents. Still another object is to provide a biaxially oriented, crosslinked, polyolefin film having micropores. A further object is to provide a crosslinked, heat-shrinkable, microporous polyolefin film.

Other objects and advantages will become apparent from a reading of the following description of the invention.

The aforestated objects are accomplished by the present invention which provides a composition of matter comprising a polyolefin selected from the group consisting of

(A) Polyethylene, polypropylene and ethylene-vinyl copolymers,
(B) 20–400% by weight by said group member of a pore-forming soild and
(C) 0.1–10% by weight by said group member of an organic compound capable of generating free-radicals, preferably an organic peroxide.

The present invention also provides a process for forming microporous crosslinked polyolefin which comprises

(1) Forming a substantially homogeneous mixture of normally solid polyolefins selected from the group consisting of polyethylene, polypropylene and ethylene-vinyl copolymers, 20–400% by weight of said group member of a pore-forming solid and 0.1–10% by weight of said group member of a free radical generating crosslinking agent,
(2) Shaping the mixture into a desired shape, e.g. sheet or film, having a thickness of 0.1 to 40 mils at temperatures sufficient to melt the polyolefin below the gel point of the mixture,
(3) Curing the shaped mixture to form a thermoset polyolefin by heating the mixture to at least the decomposition temperature of the crosslinking agent and
(4) Thereafter extracting the pore-forming solid from the polyolefin with a suitable solvent at temperatures up to the degradation temperature of the crosslinked polymer.

The following steps are considered variations of and a part of the process of the instant invention.

After step three in the above process, i.e. curing the polyolefin by heating to a higher temperature, it is sometimes desirable and often preferable to orient, uniaxially or biaxially, the polyolefin at temperatures within about 10° C. below its melting point up to its normal extrusion temperature. The addition of such a step to the process aids in removing the uneffected pore-forming solid from its expanded surroundings. After removal of the pore-forming solid, the oriented porous film can be reheated to heat shrink the film. Alternatively, it is possible to perform the orientation step after dissolving out the pore-forming solid to obtain a heat shrinkable film on reheating. This method has the advantage that the temperature employed during the extraction of the pore-forming solid can be elevated to the normal extrusion temperature of the crosslinked polyolefin without effecting subsequent orientation and heat shrinkability.

A further innovation of the instant invention is the use of irradiation instead of chemical means to crosslink the polyolefin.

The invention further provides the crosslinked, microporous, polyolefin-containing product and the crosslinked, heat-shrinkable, microporous, polyolefin-containing product in the form of sheet and film.

Although the invention relates to polyolefins selected from the group consisting of ethylene, propylene and ethylene-vinyl copolymers, for purposes of brevity the invention will be described mainly in terms of polyethylene unless otherwise noted. However, it should be understood that when the term polyethylene is used, the other polyolefin group members are meant and included. Thus, ethylene-vinyl copolymers such as ethylene-vinyl acetate, ethylene-vinyl chloride, ethylene-ethyl acrylate and the like are included in this invention.

3

The invention further provides the crosslinked, microporous polyethylene product in the form of sheet and film.

As used herein the term "pore-forming solid" means any material 0.1 to 10 microns in diameter which can be extracted from the polyethylene by selected solvents or by vacuum at a temperature below the degradation temperature of the crosslinked polyethylene. Heretofore extraction of the pore-forming solid from thermoplastic polyethylene was of necessity performed with suitable solvents at temperatures below the softening point of the polymer to avoid loss of shape of the polymer and swelling of the polymer which caused blocking of the pores. By the practice of this invention, one is able to extract the pore-forming solids at temperatures above the crystalline melting point, i.e. up to the degradation temperature of the polymer due to the fact that the polyethylene is now thermoset. Such high temperature extraction allows one to perform the extraction step at a greatly increased rate without fear of distorting the final shape of the polymer.

Similarly as used herein the term "selected solvents" means a vacuum or any solvent that will dissolve the pore-forming solid at a temperature below the degradation temperature of the crosslinked polyethylene. Examples of suitable pore-forming solids and selected solvents therefor are almost endless and will be immediately evident to those skilled in the art. Pore-forming solids and selected solvents therefor include, but are expressly not limited to, the examples in the following listing:

Pore-forming solids:	Selected solvents
Sugar; sodium chloride; Na₂CO₃·10H₂O; sodium benzoate; sodium acetate	Water.
Silica gel	Aqueous sodium hydroxide.
Starch; sugar	Dilute sulfuric acid.
Benzoic acid	Carbon tetrachloride xylene.
Hydroquinone	Ethyl alcohol; ethylene glycol.
Dimethylterephthalate; anthracene	Vacuum at 20–200° C.

The term "gel point" as used herein means the point at which a three dimensional network of molecules is formed in the polymer. When crosslinking by chemical means using a free radical generating crosslinking agent, the "gel point" means those temperatures at which there is sufficient decomposition of the crosslinking agent to cause gel formation i.e., a three dimensional network of molecules in the polymer. The gel point of any specific mixture depends upon numerous factors, including e.g., the particular polyolefin, the particular crosslinking agent, the amount of crosslinking agent, and the half-life of the crosslinking agent at various shaping temperatures. As the gel point of any specific mixture is dependent on so many factors, it is best determined by empirical methods, e.g., by extruding a small sample and observing or determining whether any gel formation is present. In a continuous operation the shaping step in the instant invention is carried out prior to crosslinking the polymer at temperatures which preclude gel formation in the polymer thus insuring against plugging of the shaping mechanism such as an extruder. Subsequent to shaping, the temperature of the shaped mixture is elevated to the gel point. In the examples herein where individual or batch samples in the form of film are processed, it is possible, if desired, to substantially shape and chemically crosslink simultaneously.

As used herein the term "decomposition temperature" of the crosslinking agent means a temperature at which the crosslinking agent has a half-life of less than about 1.0 minute and preferably less than about 0.5 minute. This can best be determined by one skilled in the art empirically.

4

Crosslinking agents do not ordinarily have a sharp decomposition point, except possibly at very high temperatures. In the usual case, the agent requires several minutes to decompose substantially quantitatively, and the rate of decomposition at a given instant is generally proportional to the amount of material. Consequently, the decomposition rate for a given material at a given temperature can generally be determined by its half-life at that temperature. The half-life of any free-radical generating agent can be readily determined by one skilled in the art. In the case of peroxides, for example, the determination involved is described in Doehnert et al., Evaluation of Organic Peroxides on the Basis of Half-Life Data, Ann. Tech. Management Conf., Reinforced Plastics Div., Soc. Plastics Ind., Inc., 13, Sect. 1–B, 1–8 (1958); Chem. Abs., 53, 19534i (1959).

Organic compounds capable of generating free radicals which are operable as crosslinking agents in the instant invention include organic peroxygen compounds and azo compounds. Suitable organic peroxygen compounds include but are expressly not limited to dicumyl peroxide, 1,2-bis(α-cumylperoxyisopropyl)benzene, 1,3-bis(α-cumylperoxyisopropyl)benzene, 1,4-bis(α-cumylperoxyisopropyl)benzene, tert-butyl perbenzoate, 1,2-bis(t-butylperoxyisopropyl)benzene, 1,3-bis(t-butylperoxyisopropyl)benzene, 1,4-bis(t-butylperoxyisopropyl)benzene, 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane and 2,5-dimethyl-2,5-di-(tert-butylperoxy)-3-hexyne. Operable azo compounds include 2-phenylazo-2,4-dimethylvaleronitrile, 2-phenylazoisobutyronitrile,2,4,4-trimethylvaleronitrile, 2-phenyl-azo-isobutyramide and the like.

The following is a list of a few of the operable crosslinking agents and their half-life.

Crosslinking agent:	Half-life
Di(tert)-butyl) peroxide	1 minute at 190° C.
Tert-butyl hydroperoxide	1 minute at 230° C.
Dichlorobenzyl peroxide	1 minute at 112° C.
Tert-butyl peracetate	0.5 minute at 178° C.
Dicumyl peroxide	0.6 minute at 182° C.
Diethyl peroxide	1 minute at 198° C.
Di(tert-amyl) peroxide	1 minute at 182° C.
Cyclohexyl peroxide	0.5 minute at 226° C.
2,5 - dimethyl - 2,5 - di - (tert-butyl-peroxy) hexane	0.6 minute at 185° C.
2,5 - dimethyl - 2,5 - di-(tert-butyl-peroxy) -3-hexyne	0.6 minute at 192° C.
α,α' - Azobis (α,γ,γ - tri-methylvalero-nitrile	2 minutes at 91° C.
α,α' - Azobis (α - cyclopropyl-proprionitrile)	1 minute at 118° C.
Dimethyl - α,α'-azodiisobutyr-ate	2 minutes at 138° C.
α,α'-Azodiisobutyronitrile	2 minutes at 132° C.
Azodicyclohexane carbonitrile	2 minutes at 166° C.
φ - hydroxyethylazo - α,γ - dimethylvalero-nitrile	2 minutes at 182° C.

The crosslinking agents can be used singly or in combination. It is only necessary that the "gel point" of the mixture be sufficiently high to enable shaping of the mixture in an extruder or other shaping mechanism at temperatures above the melting point of the polymer without crosslinking occurring.

Any of the various well-known types of polyethylene can be used in making film by the process of this invention. Such polyethylenes include the branched low-density (i.e. about .010 to about .925) material having melting points in the range 90–110° C., as well as the medium density materials and the newer linear high density (about .950 to .980) materials made by the Ziegler process (TiCl₄-Al alkyl catalyst) and the Phillips process (hexavalent chromia on silica-alumina support). The linear polyethylenes have melting points in the range of 120–

5

137° C. and therefore require peroxides (or other free-radical generating crosslinking agents) that provide gel points higher than these melting point temperatures.

The crosslinking step to form thermoset polyethylene in addition to being accomplished by chemical means can be performed by ionizing radiation of either the particle or electromagnetic type as will be shown hereinafter. Such radiation has an energy of at least about 0.01 mev. While the irradiation step to crosslink the polyethylene to gelation is preferably carried out using corpuscular particles it is also operable with X-rays or gamma rays. Thus positive corpuscular particles such as protons, alpha particles and denterons in addition to electrons and neutrons are operable to bombard the polymer.

Although the irradiation step in the examples herein used a Van de Graaff electron accelerator as the irradiation source, it should be understood that the present invention is not limited thereto. The particles may be accelerated to high speeds by means of various voltage gradient mechanisms such as a cyclotron, a Cockroft Walton accelerator, a resonant cavity accelerator, a betatron, a GE resonant transformer, a synchroton, and the like. Furthermore, particle irradiation may also be supplied from radioactive isotopes or an atomic pile. It is also possible to crosslink the polymers by the use of a sensitizer, e.g. benzophonone and U. V. light.

When irradiation is employed instead of chemical means to crosslink the polymer, the upper limit of the temperature range of the shaping step to put the polymer containing the pore-forming solid in the form of film is no longer limited to the decomposition temperature of the crosslinking agent. Thus it is possible to perform the shaping operation at temperatures ranging from the melting point of the polymer up to temperatures 150° C. in excess thereof, preferably between the melting point and 75° C. thereabove.

The amount of irradiation necessary to crosslink the polyethylene to gelation by the practice of this invention is a dose in the range of 0.1 to 100 megarads. Obviously, the dosage is dependent upon the molecular weight of the polymer prior to irradiation with a lesser dosage required for higher molecular weight polymer and vice versa.

The resultant crosslinked, microporous polyethylene product of the present invention has many and varied uses. For example, it can be used to make battery separators and the like. It is especially useful as a material having pores which will permit gases, e.g. oxygen, to pass therethrough but which are of such size as to prevent the passage of water. Thus the product would be useful as a raincoat or covering such as a tent or the like which allowed one to breathe oxygen without permitting the countercurrent passage of rainwater. The product is also useful in situations requiring high resistance to solvents at elevated temperatures such as a filter sheet.

The following examples are set down to illustrate the invention and are not to be deemed limiting in scope.

Throughout the instant invention the melt index (MI) of the polymer was measured under the conditions specified in ASTM D 1238–52T.

The density of the polymer was measured under the conditions specified in ASTM D 1505–57T.

The percent gel content of the crosslinked film in the instant invention was measured by refluxing a weighed sample (approximately 0.5 g.) of film in a cellulose Soxhlet thimble in xylene (containing 0.3 weight percent 2,6-ditertiary-butyl-4-methyl-phenol, commercially available under the tradename "Ionol" from Shell Oil Corp.) for 24 hours. The insoluble portion of the sample after drying was weighed to calculate percent gel as follows:

$$\text{Percent gel} = \frac{\text{weight insoluble sample}}{\text{total weight sample}} \times 100$$

In general the procedure followed for forming chemically crosslinked microporous polyethylene in the exam-

6

ples was to compound the polyethylene, pore-forming solid and crosslinking agent on a Brabender Plastograph, Banbury Mixer or two-roll mill at a temperature about 10–30° C. above the melting point of the polymer but below the gel point for about 5–20 minutes. It is also possible to admix the reactants, preferably in particulate form, at temperatures below the melting point of the polymer, e.g. 25° C. and thereafter heat the mixture above the melting point of the polyethylene to form a homogeneous mixture in the molten polymer. It is also sometimes preferred, especially where there is concern with premature crosslinking in the mixing or compounding step, to admix solely the polyethylene and the pore-forming solid at temperatures whereat the polymer is molten until a homogeneous mixture is realized e.g. about 10 minutes, and thereafter add the crosslinking agent with continued mixing for an additional 1–5 minutes. This decreases the possibility of premature crosslinking in the compounding step since the crosslinking agent is not exposed to an elevated temperature for so long a period. For shaping, samples of the mixture, (approximately 10–40 gms. in weight) were pressed into films of about 10–20 ml. thickness using a platen press at temperatures whereat the polymer is molten but below the decomposition temperature of the crosslinking agent. The film samples were then cured in the press for 10–30 minutes at 20,000 p.s.i. at temperatures above the gel point. After curing, the self-supporting film samples were transferred to a tank containing a selected solvent for the extraction of the pore-forming solid. For example, when starch is used as the pore-forming solid, the solvent in the tank is dilute sulfuric acid maintained at a temperature of 99–100° C. Due to the ability to employ a high temperature without detriment to the thermoset polymer, the extraction step is shortened considerably. Extraction periods of 10 min. to 3 hrs. are sufficient to leach the pore-forming material out of the polymer. The polymer is then washed to remove the solvent therefrom. Samples of the cured, microporous polyethylene film were taken to calculate the percent gel content by the aforestated xylene extraction method. The porosity of the polymer was characterized by its permeability to oxygen and water vapor.

In the process where the polymer is crosslinked by irradiation, the compounding of the polyethylene and pore-forming solid is performed at temperatures whereat the polymer is molten e.g. 10–75° C. above the melting point of the polymer. The homogeneous admixture is shaped e.g., in the form of sheet or film under pressure on a platen press or in an extruder and cooled. The shaped admixture is irradiated with a dosage of 0.5–100 megarads to crosslink the polymer. The pore-forming solid is extracted with a selected solvent as mentioned supra for the chemical crosslinking procedure.

Example 1

100 parts of commercially available polyethylene (density 0.91; melt index 2.0) and 30 parts of commerically available powdered cane sugar as a pore-forming solid having an average diameter of 2 microns were compounded on a two roll mill at about 135° C. until a homogeneous mixture was obtained. Films of 1–3 mils thickness were pressed on a platen press at about 135–140° C. The films were cooled. Samples of the films were crosslinked by irradiation at dosages of 8 and 12 megarads with a Van de Graaff electron generator. The crosslinked films were immersed in a 3½% solution of sulfuric acid at a temperature of 99° C. for 60 minutes to extract the sugar from the polymer. This bath was followed by a bath of distilled water to remove the acid with subsequent drying of the film samples. On characterization the film samples irradiated at a dosage of 8 megarads had a gel content of 59% and those subjected to a dosage of 12 megarads had a gel content of 68%. The crosslinked microporous polyethyiene produced by

7

the aforementioned treatment contained pores ranging in size from 1 to 4 microns in diameter with an average pore size of about 2 microns. To show the decreased solubility of the crosslinked microporous product, samples thereof were immersed in a bath of a mixture of 50% xylene and 50% benzene at 80° C. for 3 hours. Control samples of the same polyethylene which had not been subjected to crosslinking were also placed in the solvent bath. At the end of 3 hours the uncrosslinked polyethylene had completely dissolved in the solvent while the cross-linked microporous polyethylene showed only swelling and on drying recovered its shape.

Example 2

Example 1 was repeated except that the commercially available polyethylene used had a density of 0.96 and a melt index of 0.7. The extraction of the sugar was performed by immersing the crosslinked film in a 3½% solution of sulfuric acid at a temperature of 99° C. for 90 minutes. The resultant microporous product irradiated with a dosage of 8 megarads had a gel content of 22% and the sample subjected to a 12 megarad dosage had a gel content of 35%. The crosslinked, microporous, high density polyethylene recovered its shape on drying after 5 hours at 100° C. in a bath of 100% xylene. The control sample of the polyethylene which had not been cross-linked was completely dissolved.

Example 3

Example 1 was repeated except that 100 parts of starch 3–7 microns average diameter, was used as the pore-forming solid with the 100 parts of polyethylene. The resultant crosslinked microporous product recovered its shape on drying after 5 hours in a bath of 50% xylene and 50% benzene at 80° C. A control sample which was not subjected to crosslinking by irradiation was dissolved in the xylene-benzene bath within 3 hours.

Example 4

100 parts of commercially available polyethylene (density 0.91; melt index 2.0) and 200 parts of silica gel as a pore-forming solid having an average diameter of 3–7 microns were compounded on a two roll mill at about 135° C. until a homogeneous mixture was obtained. 1.0 part of 2,5-dimethyl-2,5-di(t-butylperoxy)-3-hexyne peroxide in a benzene solution were then added as a crosslinking agent to the mixture and compounding was continued for 3 minutes. The mixture was removed from the two roll mill and samples thereof were pressed on a platen press into 10 mil thick film at 130° C., followed by a twenty minute cure in the press at 175° C. and 20,000 p.s.i. pressure. The cured film samples were then immersed for 3 hours in a 50% solution of NaOH at a temperature of 99° C. to leach the silica gel out of the polymer. After washing with distilled water, the samples were dried overnight at 50° C. On characterization the crosslinked microporous polyethylene film had a gel content of 60% and contained pores ranging in size from 2 to 7 microns in diameter. The crosslinked microporous polyethylene film recovered its shape on drying after immersion in a bath of 50% xylene and 50% benzene at 80° C. for 6 hours.

Example 5

Example 4 was repeated except that the commercially available polyethylene had a density of 0.96 and a melt index of 0.7 and the crosslinking agent consisted of 0.75 part of 2,5-dimethyl-2,5-di(tert-butylperoxy) - 3 - hexyne. Characterization showed that the crosslinked, microporous polyethylene film had a gel content of 40% and contained pores ranging in size from 3 to 6 microns in diameter. The resultant crosslinked microporous product was immersed in a bath of 100% xylene at 1000 C. After 5 hours the crosslinked microporous polyethylene showed swelling and on drying recovered its shape.

8

The following examples show the inclusion of the biaxial orientation step in the invention.

Example 6

100 parts of commercially available polyethylene (density 0.91; melt index 2.0) and 15 parts of commercially available powdered cane sugar as a pore-forming solid having an average diameter of 2 microns were compounded on a Brabender Plastograph at a temperature of 140° C. until a homogeneous mixture was obtained. The mixture was removed from the Brabender Plastograph and pressed into films of 20 mil thickness at 350° F. on a platen press. The films were cooled. Samples of the pressed film were crosslinked by irradiation at a dosage of 8 megarads with a Van de Graaff electron generator. The thus irradiated film samples were then biaxially oriented under 5 lbs. air pressure at a temperature of 120° C. until it had an elongation ratio of 4×. A sample of the biaxially oriented film was accurately weighed and placed in a water bath at 40° C. for 1 hour to extract the pore-forming solid. The crosslinked, microporous polyethylene produced by the aforementioned treatment contained pores ranging in size from 6 to 10 microns in diameter with an average pore size of about 8 microns. The heat-shrinkable film was shrunk by reheating it to 100° C. to shrink the film to substantially its original size. Remeasurement of the pores of the film showed that the pores ranged in size from 1 to 3 microns in diameter with an average pore size of about 2 microns.

Example 7

100 parts of commercially available ethylene-propylene copolymer containing 70% ethylene by weight and having a density of 0.928 and 30 parts of commercially available powdered cane sugar as a pore-forming solid having an average diameter of 2 microns were compounded on a Brabender Plastograph at 180° C. until a homogeneous mixture was obtained. The mixture was removed from the Brabender and pressed on a platen press at 400° F. to form 20 mil thickness film. The thus formed film were crosslinked by irradiation and a dosage of 8 megarads with a Van de Graaff electron generator. The thus irradiated film samples were then biaxially oriented under 5 lbs. air pressure until it had an elongation ratio of 3×. The thus crosslinked, oriented copolymer film was immersed in a 3½% solution of sulfuric acid at a temperature of 99° C. for 60 minutes to extract the sugar from the copolymer. This bath was followed by a bath in distilled water to remove the acid with subsequent drying of the film samples. On characterization the film samples had a gel content greater than 15%. The crosslinked, biaxially oriented, microporous copolymer contained pores ranging in size from 4 to 8 microns in diameter with an average pore size of 6 microns. The film sample was reheated at 165° C. to heat shrink the film. Reexamination of the heat-shrunked film showed that the average pore size was about 2 microns.

Example 8

Example 7 was repeated except that commercially available polypropylene having a density of 0.91 was substituted for the copolymer. The Brabender temperature was 185° C. The mixture was removed from the Brabender and pressed into films of about 20 mil thickness on the platen press at about 180° C. The films were cooled. Samples of the pressed film were crosslinked by irradiation at a dosage of 20 megarads with a Van de Graaff electron generator and then heated for 5 minutes at 150° C. The thus crosslinked film was then biaxially oriented under 5 pounds air pressure at 150° C. until it had an elongation ratio of 3×. The crosslinked films were immersed in a 3½% solution of sulfuric acid at a temperature of 99° C. for 60 minutes to extract the sugar from the polymer. This bath was followed by a bath in distilled water to remove the acid with subsequent drying of the film sam-

ples. On characterization the film samples contained pores ranging in size from 4 to 8 microns and an average pore size of about 6 microns. The film was reheated to 165° C. thereby yielding microporous film having an average pore size of 2 microns.

On repeating the example except that the crosslinking by irradiation and heating was omitted, the biaxial orientation resulted in an elongation ratio of 4×. After extraction of the sugar, the film contained pores ranging in size from 6 to 10 microns with an average pore size of about 8 microns. On reheating the film to 160° C. the average pore size was 2 microns.

Example 9

100 parts of commercially available polyethylene density of 0.91; and a melt index 2.0 and 30 parts of commercially available powdered cane sugar as a pore-forming solid having an average diameter of 2 microns were compounded on a two roll mill at about 130° C. until a homogeneous mixture was obtained. Films of 20 mil thickness were pressed on a platen press at about 135° C. Samples of the pressed films were crosslinked by irradiation at a dosage of 8 megarads with a Van de Graaff electron generator. The crosslinked films were washed with a 3½% solution of sulfuric acid at a temperature of 99° C. for 60 minutes to extract the sugar from the polymer. The films contained pores ranging in size from 1 to 3 microns in diameter. The films were then biaxially oriented at a temperature of 100° C. and 5 lbs. air pressure until the film had an elongation ratio of 4×. On characterization the thus biaxially oriented crosslinked films contained pores ranging in size from 6 to 10 microns in diameter with an average pore diameter size of 8 microns. On reheating the film to 95° C. the pores ranged in size from 1 to 3 microns in diameter with an average pore size of about 2 microns.

Example 10

100 parts of commercially available polyethylene having a density of 0.96 and a melt index of 5.0 and 30 parts of commercially available powdered cane sugar as a pore-forming solid having an average diameter of 2 microns were compounded on a Brabender Plastograph at a temperature of 140° C. until a homogeneous mixture was obtained. 1.0 part of 1,4-bis(t-butylperoxyisopropyl) benzene was then added as a crosslinking agent to the mixture and compounding was continued for 2 minutes. The mixture was removed from the Brabender and samples thereof were pressed on a platen press into 20 mil thick film at 150° C. followed by a 20 minute cure in the press at 175° C. and 20,000 p.s.i. pressure. The cured film samples were then biaxially oriented under 5 lbs. air pressure until they had an elongation ratio of 4×. The biaxially oriented films were then immersed in a 3½% solution of sulfuric acid at a temperature of 99° C. for 60 minutes to extract the sugar from the polymer. This bath was followed by a bath in distilled water to remove the acid with subsequent drying of the film samples. On characterization the film samples contained pores ranging in size from 4 to 8 microns with an average pore size of about 6 microns. The films were reheated to 130° C. thereby yielding crosslinked microporous film having an average pore size of 2 microns.

The following examples shows the operability of ethylene-vinyl copolymers in the instant invention.

Example 11

100 parts of a commercially available copolymer of ethylene-vinylacetate sold under the tradename "Elvax" containing 33 weight percent of vinylacetate, having a melt index of 25 and a density of 0.957 and a softening point of 115° C. in accord with ASTM D–28 and 30 parts of a commercially available powdered cane sugar as a pore-forming solvent having an average diameter of 2 microns were compounded on a Brabender Plasto-

graph at a temperature of 140° C. until a homogeneous mixture was obtained. Films of 20 mils thickness were pressed on a platen press from the thus formed mixture at about 135° C. Samples of the pressed films were crosslinked by irradiation at a dosage of 8 megarads with a Van de Graaff electron generator. The thus crosslinked films were then biaxially oriented under 5 lbs. air pressure at 105° C. until they had an elongation ratio of 3×. The crosslinked, biaxially oriented films were immersed in a 3½% solution of sulfuric acid at a temperature of 99° C. for 60 minutes to extract the sugar from the polymer. This bath was followed by a bath in distilled water to remove the acid with subsequent drying of the film samples. On characterization the film samples contained pores ranging in size from 4 to 8 microns and an average pore size of about 6 microns. The film was reheated to 125° C. thereby yielding microporous film having an average pore size of 2 microns.

Example 12

Example 11 was repeated except that 100 parts of a commercially available ethylene-ethyl acrylate copolymer sold under the tradename "Zetafin" having a density of 0.929 and a melt index of 18.5 was substituted for the ethylene-vinyl acetate copolymer. On characterization, the irradiated, biaxially oriented film samples contained pores ranging in size from 4 to 8 microns and an average pore size of about 6 microns in diameter. The film on reheating to 125° C. yielded a crosslinked, microporous film having an average pore size of 2 microns in diameter.

What is claimed is:

1. A process for forming crosslinked oriented microporous, polyolefin film containing a plurality of pores having an average diameter of 0.1 to 10 microns which comprises forming a mixture consisting essentially of a polyolefin member of the group consisting of polyethylene, polypropylene and ethylene-vinyl copolymers, 20–400% by weight of said polyolefin group member of a finely divided pore-forming solid having an average diameter in the range 0.1 to 10 microns and 0.1 to 10% by weight of said polyolefin group member of an organic compound capable of generating free radicals, heating the mixture to above the melting point of the polyolefin group member but below the decomposition temperature of the organic compound, shaping the thus heated mixture in the form of film, crosslinking the shaped mixture by heating to at least the decomposition temperature of the organic compound, orienting the crosslinked film at a temperature within about 10° C. below its melting point up to its normal extrusion temperature and thereafter extracting the pore-forming solid at a temperature below the degradation temperature of the crosslinked polyolefin group member.

2. The process according to claim 1 wherein the polyolefin group member is oriented after extracting the pore-forming solid.

3. A process for forming crosslinked oriented microporous polyolefin film containing a plurality of pores having an average diameter of 0.1 to 10 microns which comprises forming a mixture consisting essentially of a polyolefin member of the group consisting of polyethylene, polypropylene and ethylene-vinyl copolymers and 20 to 400% by weight of said polyolefin group member of a finely divided pore-forming solid having an average diameter of 0.1 to 10 microns, heating the mixture to a temperature ranging from the melting point of the polyolefin group member up to 150° C. in excess thereof, shaping the heated mixture in the form of film, crosslinking the shaped mixture by irradiating with ionizing irradiation with a dosage of 0.1 to 100 megarads orienting the crosslinked film at a temperature within about 10° C. below its melting point up to its normal extrusion temperature and thereafter extracting the pore-forming solid at a temperature below the degradation temperature of the crosslinked polyolefin group member.

4. The process according to claim **3** wherein the polyolefin group member is oriented following the extraction of the pore-forming solid.

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MURRAY TILLMAN, *Primary Examiner.*

SAMUEL H. BLECH, *Examiner.*

J. C. BLEUTGE, *Assistant Examiner.*